

**NON-TOXIC CORROSION-PROTECTION
CONVERSION COATS BASED ON RARE EARTH ELEMENTS**

CROSS-REFERENCE TO RELATED APPLICATIONS

5 This application is a continuation-in-part of commonly assigned U.S. Application Serial No. 10/038,274, filed January 4, 2002 and entitled “NON-TOXIC CORROSION-PROTECTION CONVERSION COATS BASED ON COBALT.” This application is also related to U.S. Application Serial No. ____ /____, ____ (Attorney Docket No. UVD 0279 IA), filed ____ __, 2003 and entitled “NON-TOXIC CORROSION-PROTECTION PIGMENTS BASED ON RARE 10 EARTH ELEMENTS”, which is a continuation-in-part of U.S. Application Serial No. 10/037,576, filed January 4, 2002 and entitled “NON-TOXIC CORROSION-PROTECTION PIGMENTS BASED ON COBALT”, and U.S. Application Serial No. ____ /____, ____ (Attorney Docket No. UVD 0299 IA), filed ____ __, 2003 and entitled “NON-TOXIC CORROSION-PROTECTION RINSES AND SEALS BASED ON RARE EARTH ELEMENTS”, which is a 15 continuation-in-part of U.S. Application Serial No. 10/038,150, filed January 4, 2002 and entitled “NON-TOXIC CORROSION-PROTECTION RINSES AND SEALS BASED ON COBALT”, the disclosures of which are incorporated herein by reference.

BACKGROUND OF THE INVENTION

20 This invention relates generally to compositions and methods for the formation of protective, corrosion-inhibiting coatings on metals, or other materials coated with metals, without the use of chromium in the hexavalent oxidation state. More particularly, this invention relates to non-toxic, corrosion-inhibiting conversion coatings based on tetravalent cerium, praseodymium, or terbium and methods of making and using the same.

25 Metals like aluminum, zinc, magnesium, titanium, cadmium, silver, copper, tin, lead, iron, rare earths, zirconium, beryllium, niobium, tantalum, lithium, or indium, their alloys, or items coated with these metals, tend to corrode rapidly in the presence of water due to their low oxidation-reduction (redox) potentials or ease of oxide formation. Non-alloyed specimens of these metals typically form a natural oxide film that will protect them somewhat and reduce their overall rate of corrosion. However, alloys of these metals are particularly sensitive to corrosive 30 attack. These materials also have a significant problem with paint adhesion. The as-formed

metal surfaces are typically very smooth, and they tend to form weakly bound surface oxides. The native oxides do not normally provide a robust base on which subsequent paints can anchor themselves. These metal alloys have many uses ranging from architectural adornments, to protective coatings on ferrous alloys, to structural aerospace components, *inter alia*.

5 The 2000 and 7000 series of aluminum alloys are used throughout military and civilian aircraft because of their high strength to weight ratio. However, these aluminum alloys are very sensitive to corrosive attack because their natural oxide layer offers only a limited degree of protection. Materials with greater redox potentials, such as steels or carbon fibers, in proximity to aluminum alloys will promote corrosive attack in water by the formation of a galvanic

10 corrosion couple with the less-noble light metal alloy.

Inhibiting the initiation, growth, and extent of corrosion is a significant part of component and systems design for the successful long-term use of metal objects. Uniform physical performance and safety margins of a part, a component, or an entire system can be compromised by corrosion.

15 One method of enhancing the corrosion resistance of these alloys includes the use of a conversion coating. A conversion coating is a self-healing, corrosion-inhibiting layer formed during intentional exposure to a chemically reactive solution. The conversion coating process forms an adherent surface containing an integral corrosion inhibitor with “throwing power” that can provide protection to coating breaches. The metal is exposed to a compound that chemically

20 alters the surface and forms a coating that provides a high degree of corrosion resistance. A chemical conversion coating applied to the surface of a less-noble alloy can reduce the extent and severity of aqueous corrosion, provide long-term property stability, and extend the useful life of the object of manufacture.

Conversion coatings incorporate a portion of the base metal and form a mechanical, chemical, and electrostatic barrier to corrosive attack. A feature of effective conversion coatings is their ability to provide corrosion protection to the base metal in the presence of a coating breach.

Anodization of a metal surface followed by “sealing” or “rinsing” of the anodized metal does not constitute the formation of a conversion coating in our usage. Anodization, the

30 formation of a porous oxide film on the metal, is achieved by the application of an electrical potential to the metal. This oxide film must then be “sealed”, “washed”, or “rinsed” in order to

impart complete corrosion protection. Typically, the corrosion protection afforded by an anodized piece is due to the barrier oxide film. Conversion coatings, however, grow an oxide coating on the metal without an externally applied electrical potential. The protective film is produced by a chemical redox reaction between the metal surface and the conversion coating solution. The film is composed both of an oxide and integral corrosion inhibitor species formed during exposure to the conversion coating solution. A true conversion coating therefore affords corrosion protection from an oxide barrier film that has co-deposited oxidative corrosion inhibitor species.

A conversion-coated surface may be left bare or afforded further protection by the application of additional films or coatings. Conversion coatings need to adhere to the substrate and should result in a surface that will promote the formation of a strong bond with subsequently applied coatings. Bonding with subsequently applied coatings is a function of the morphology and chemical composition of the conversion coating. Adhesion promoting surface treatments may exhibit corrosion-inhibiting characteristics. Depending on the intended application, a conversion coating, as described herein, may be considered to be an “adhesion promoter” and vice versa.

Conversion coatings are usually formed by the application of a conversion coating solution to a metal surface. The solution can be applied by immersion, spray, fogging, wiping, or other means.

Hexavalent chromium has traditionally been used in the formation of protective conversion coatings for aluminum, zinc, magnesium, titanium, cadmium, silver, copper, tin, lead, iron, rare earths, zirconium, beryllium, indium, and their alloys. Compounds such as Alodine® (available from Henkel Surface Technologies, Madison Heights, MI) and Alumigold™ (available from Turco Products, Inc., Madison Heights, MI) contain hexavalent chromium as their main corrosion-inhibiting compound.

Two generic types of hexavalent chromium coatings have been widely used. The newer “gold” coatings are named for the faint gold tint that is exhibited when these coatings form on the surface of aluminum alloys. The compositions and application procedures of these “gold” hexavalent chromium conversion coating formulations are described in United States military process specifications, as well as other federal guidelines. Therefore, guidelines for the application of these solutions to aluminum (MIL C-5541; MIL C-81706; MIL STD-171; ASTM

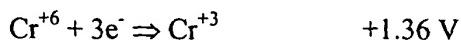
B-449), zinc (ASTM B-633; ASTM B-201; MIL C-17711; QQ Z-325a), magnesium (MIL M-3171), cadmium (ASTM A-165; ASTM B-201; QQ P-416b), silver (ASTM B-700; QQ S-365a), copper (ASTM B-281), and tin (ASTM A-599; QQ-T-425a) are available. The common components to these "gold" conversion coating baths are hexavalent chromium, complex fluorides, and ferricyanide. Older "green" conversion coatings containing hexavalent chromium have also been described, and the color formed on aluminum alloys through the application of these conversion coatings is a light green color. The "green" formulations all contain hexavalent chromium, a fluoride, and an acidic phosphate component. The major compositional difference between the two is that the current "gold" formulation contains ferricyanide and the older "green" formulations contain phosphate.

Corrosion-resistant compositions have also been described which contain hexavalent chromium, fluoride, and molybdic acid or molybdates, rather than ferricyanide or phosphate. Tungstates and vanadates have also been used in combination with hexavalent chromium and fluoride. Hexavalent chromium formulations which do not contain a fluoride source, and which contain borate ions instead of ferricyanide or phosphate or molybdate have also been described. Hexavalent chromium has also been used in combination with stannates, oxalates, and tellurates. Finally, corrosion protection of aluminum, magnesium, or zinc alloys has been achieved through the use of hexavalent chromium, fluoride, and rare earth compounds.

The variation in the type and amount of additional components such as ferricyanide, phosphate, molybdate, and borate, etc., in conversion coat formulations based on hexavalent chromium is significant in light of the chemistry developed and presented in the present invention. It is important to note that hexavalent chromium conversion coatings which have nearly identical formulations, except for one or more of the non-chromium components, result in obvious differences on the applied metal surface for a given alloy (such as "gold" and "green" coatings). It is also important to note that differences in the composition of aluminum alloys will influence the chemistry of the conversion coating formed when only one hexavalent chromium conversion coat composition is used.

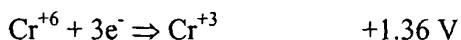
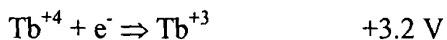
Significant efforts have been made to replace chromium with other metals for corrosion-inhibiting applications due to toxicity, environmental, and regulatory concerns. Cerium is one non-toxic, non-regulated metal which has been considered as a chromium replacement. Cerium (like chromium) exhibits more than one oxidation state (Ce^{+3} and Ce^{+4}). In addition, the

oxidation-reduction potential of the Ce^{+4} - Ce^{+3} couple is comparable to the Cr^{+6} - Cr^{+3} couple. For example, in acid solution:



Praseodymium and terbium also exhibit more than one oxidation state (Pr^{+3} and Pr^{+4} , Tb^{+3} and Tb^{+4}). Tetravalent praseodymium and terbium are even stronger oxidizing agents than cerium (with calculated redox potentials of +3.3 V in acidic solution (Nugent, L.J., et al., *J.*

Inorg. Nucl. Chem. 33: 2503-30, 1971):



A number of processes have been reported in the literature that make use of cerium in conversation coating bath solutions, as well as general corrosion protection or coloring of the alloys. However, the coatings formed by these processes provide only limited protection and do not approach the benefit derived from the use of hexavalent chromium.

The use of film-forming substances, such as polymers, silicates, sol-gel, etc., which have no inherent oxidizing character, in conversion coating solutions has been described in the literature. The film formers may enhance short-term corrosion resistance by functioning as a barrier layer. However, these films interfere with substrate oxidation during the conversion coating process and produce thin, incompletely anodized surfaces, resulting in poor mechanical adhesion to the solution-deposited polymer film and to later applied coatings. Restricting the formation of the oxide layer that acts as a reservoir for the active corrosion inhibitor yields a barrier film that is inhibitor starved. Barrier layers lacking an active corrosion inhibitor have been demonstrated to be capable of inhibiting corrosion only as long as the barrier is not breached, as by a scratch or other flaw. Film formers can actually enhance corrosion on a surface after failure due to the well-known effects of crevice corrosion. The addition of polymer during conversion coating also produces a smooth coating which can reduce subsequent paint adhesion, resulting in reduced long-term corrosion protection.

Likewise, a myriad of inorganic oxide, phosphate, silicate, carbonate, oxalate, molybdate, tungstate, zirconate, titanate, borate, etc. barrier films have been described in the literature as providing corrosion protection. However, these films will serve this function so long as the film

or coating is not breached to expose bare metal. Should this occur, none of these coatings exhibit "self-healing" characteristics. For example, hexavalent molybdenum (Mo^{+6}) found in molybdate or heteropolymolybdate coatings does not exhibit oxidation-reduction potentials comparable to hexavalent chromium (i.e., in acidic media, $\text{Mo}^{+6} + 3\text{e}^- \Rightarrow \text{Mo}^{+3}$, potential is +0.43 V; or $\text{Mo}^{+6} + 2\text{e}^- \Rightarrow \text{Mo}^{+4}$, potential is +0.65 V). Similarly, hexavalent tungsten (W^{+6}) found in tungstate or heteropolytungstate coatings does not exhibit oxidation-reduction potentials comparable to hexavalent chromium (i.e., in acidic media, $\text{W}^{+6} + 2\text{e}^- \Rightarrow \text{W}^{+4}$, potential is -0.12 V). In order to match the oxidation-reduction potential of hexavalent chromium, tetravalent cerium must be present in the coating.

U.S. Patent Nos. 5,635,084, 5,582,654 and 5,194,138, all to Mansfield et al., describe methods for treating the surface of an aluminum alloy having a relatively high copper content, so as to make the surface resistant to corrosion. The method comprises a) removing substantially all of the copper from the surface of the alloy, b) contacting the surface with a first solution containing cerium, c) electrically charging the surface while contacting with an aqueous molybdate solution, and d) contacting the surface with a second solution containing cerium. However, tetravalent cerium is not disclosed.

European Application No. EP 0 792 922 A1, by The Boeing Company et al., describes chromate-free, corrosion-inhibiting coatings for protection of aluminum and its alloys comprising a) a film-forming organic polymeric and/or sol-gel component, b) an ester of a rare earth metal, i.e., cerium, or a vanadate salt of an alkali or alkaline earth metal, and c) a borate salt of an alkali earth metal. The film-forming organic polymeric or sol-gel component may provide short-term corrosion resistance by functioning as a barrier layer. However, these films usually interfere with substrate oxidation during the conversion coating process and result in thin, incompletely anodized surfaces, resulting in poor mechanical adhesion to the solution-deposited polymer film and to later applied coatings. Polymers added during the coating process also produce smooth coatings with a limited amount of "rough" surface morphology for subsequent paint adhesion resulting in reduced long-term corrosion protection. Neither the importance of tetravalent cerium nor the functional parameters for tetravalent cerium-containing complexes are described.

Similarly, U.S. Patent No. 5,192,374 to Kindler describes the formation of an aluminum oxide (boehmite) coating on structural aluminum, followed by treatment with a soluble cerium

salt and a metal nitrate at 70°C to 100°C to form cerium oxides and hydroxides for increased corrosion resistance. The formed oxides and hydroxides are described as filling the pores in the boehmite coating. Also, Stoffer et al. in U.S. Patent No. 5,932,083 describe the use of a solution containing cerium and an oxidizing agent for treatment of aluminum alloys. The aluminum-containing substrate is electrolyzed in this solution, forming a mixed aluminum oxide/cerium oxide (or hydrated cerium oxide) coating on the aluminum as a barrier film. The formation of tetravalent or hydrated tetravalent cerium oxide is described. However, neither Kindler nor Stoffer et al. teach the use of “valence stabilizers”, which are important for use of tetravalent cerium compounds having aqueous solubilities that are sufficiently high to ensure long-term self healing of the coating. The cerium oxides and hydrated oxides described in these patents function merely as pore-filling barrier layers and not as active self-healing inhibitors within the coating. Moreover, the use of tetravalent cerium oxides and hydroxides as corrosion inhibitors results in lower corrosion performance, as is described herein, due to the fact the electrostatic double layers around such oxide and hydroxide species are much smaller than those exhibited by tetravalent cerium species containing 50% or less oxide or hydroxide as attached ligands.

Similarly, PCT International Publication No. WO 88/06639 by the Commonwealth of Australia and U.S. Patent No. 6,022,425 to Nelson et al. describe the application of a corrosion-resistant coating for aluminum based on cerium, which cerium is oxidized to the tetravalent oxidation state, resulting in the formation of tetravalent or hydrated cerium oxides. However, these references teach tetravalent cerium compounds having aqueous solubilities that are so low they function as barrier films or sealants, rather than active corrosion inhibitors. Moreover, the use of valence stabilizers for forming complexes with tetravalent cerium is not disclosed.

European Patent Application No. EP 0 902 103 A1 by Nippon Steel Corporation describes the application of a trivalent cerium solution with organic oxoacids to aluminum or galvanized steel. U.S. Patent No. 6,190,780 B1 to Shoji et al. describes the use of rare earth and/or Group IVA solutions for the treatment of metal surfaces with oxyacids (i.e., molybdates, tungstates, vanadates, or phosphates). Likewise, U.S. Patent No. 6,200,672 B1 to Tadokoro et al. describes the use of rare earth and/or Group IVA solutions with selected organic molecules for treatment of metal surfaces. U.S. Patent No. 5,964,928 to Tomlinson describes the use of a Group IVA compound (i.e., zirconium, titanium, or hafnium) in combination with a rare earth element and optionally a fluoride. Also, U.S. Patent No. 6,503,565 B1 to Hughes et al. describes

the use of aqueous acidic, rare earth ion-containing coating solutions for metal surfaces. The coating solutions can include rare earth cations capable of having more than one valence state. However, none of these references teach the presence of a valence stabilized, oxidized rare earth element such as cerium, praseodymium, or terbium in the formed conversion coating, whose availability to the corroding system is controlled via the solubility of the oxidized rare earth compounds. In order to function as a true replacement for hexavalent chromium, which is itself a highly oxidized species, the rare earth compound must be oxidized in the formed coating.

5 U.S. Patent No. 6,206,982 B1 to Hughes et al. describes the use of a four component system to provide corrosion protection of aluminum. One of these components includes a rare 10 earth compound, especially cerium.

10 The use of colloidal suspensions of tetravalent cerium oxide (CeO_2) in anticorrosive coatings is described in U.S. Patent Nos. 5,733,361 and 5,922,330 to Chane-Ching et al.; PCT International Publication No. WO 96/26255 by Rhone-Poulenc Chimie; and PCT International Publication Nos. WO 01/36331 A1 and WO 01/38225 A1 by Rhodia Terres Rares. The CeO_2 exhibits a solubility that is too low for effective release of corrosion-inhibiting tetravalent cerium 15 ions.

20 An aqueous dispersion of a cerium compound with other rare earths, transition metals, aluminum, gallium, or zirconium is described for anticorrosive agents in PCT International Publication No. WO 01/55029 A1 by Rhodia Terres Rares. Similarly, an aqueous dispersion of cerium oxide in combination with additives such as beta-diketones, alpha-hydroxycarboxylic acids, beta-hydroxycarboxylic acids, or diols is described for anticorrosive agents in U.S. Patent 25 No. 6,033,677 to Cabane et al. Neither of these references defines the need for cerium to be in the tetravalent oxidation state to achieve anticorrosive effects.

30 U.S. Application Publication No. 2003/0024432 A1 by Chung et al. describes an anti-corrosive surface treatment comprising, *inter alia*, an organometallic compound that can include cerium (i.e., cerium acetate hydrate, cerium acetylacetone hydrate, cerium 2-ethylhexanolate, i-propoxycerium, cerium stearate, and cerium nitrate). The disclosed coating is an anti-corrosive sol-gel that produces an adhesive film interface between a metal surface and an organic matrix resin or adhesive. In addition, U.S. Application Publication No. 2003/0019391 A1 by Kendig describes a corrosion inhibitor comprising an oxo-anion and a cation that is capable of inhibiting the propagation of pit corrosion on the surface of coated metal substrates. The cation can be a

rare earth metal including cerium and praseodymium, *inter alia*. However, neither Kendig nor Chung et al. describe the need for cerium to be in the tetravalent oxidation state for corrosion inhibition.

Accordingly, a need exists for improved corrosion-protection conversion coatings
5 composed of currently unregulated and/or non-toxic materials which have an effectiveness, ease of application, and performance comparable to coatings formed with hexavalent chromium, and for methods of making and using the same.

SUMMARY OF THE INVENTION

This need is met by the present invention which represents a significant improvement in
10 the formulation of non-toxic conversion coatings through the use of tetravalent cerium, praseodymium, or terbium. Although the present invention is not limited to specific advantages or functionality, it is noted that the conversion coatings of the present invention inhibit corrosion to a higher degree than any other known cerium-based coatings. Moreover, the coatings inhibit
15 corrosion to a degree comparable to commercial formulations based on hexavalent chromium. They do not require the use of elevated temperatures, or exotic materials or application methods.

The present invention utilizes “valency stabilization” of the tetravalent cerium, praseodymium, or terbium ions in the as-formed conversion coatings to achieve corrosion resistance that is comparable to hexavalent chromium. More specifically, in order to achieve a
20 high degree of corrosion resistance, a conversion coating can exhibit the following characteristics:

- 1) The coating can contain an oxidizing species. Oxidizing species serve two important functions within the coating: a) they act to impede the flow of charged species through the
25 coating, therefore helping reduce the transport of corrosion reactants, and b) if a scratch is formed in the coating, these oxidizing species act to “repair” the breach by oxidizing the underlying metal and quickly reforming an oxide barrier. The effectiveness of oxidizing species is a function of their individual oxidation-reduction potential, and the more highly oxidized species exhibit greater corrosion protection. An oxidation-reduction potential of approximately +0.80 V (at a pH of 0) appears to be the dividing line between inhibitors that offer some
30 corrosion protection and those that do not. The tetravalent cerium ion, with an oxidation-

reduction potential of +1.72 V (at a pH of 0), is an exceptionally good oxidizing species. The hydroxyl and oxygen liberated from water when tetravalent cerium is reduced will oxidize (“passivate”) nearby bare metal. Tetravalent praseodymium or terbium, with oxidation-reduction potentials of approximately +3.2 V, are even stronger oxidizers that exhibit an even higher
5 tendency to passivate nearby metal.

2) A “valence stabilizer” for the tetravalent cerium, praseodymium, or terbium can be employed to ensure that the ion will not be reduced quickly to the trivalent state in solution or in the coating. The importance of stabilizing the cerium ion in its tetravalent state in a solid
10 precipitate was not previously recognized as important to the formation of a conversion coating.

3) The tetravalent cerium, praseodymium, or terbium species formed in the coating should be present as a “sparingly soluble” material. If the formed tetravalent cerium, praseodymium, or terbium species is too soluble, then it will be washed away. If it is too insoluble, then
15 insufficient tetravalent cerium, praseodymium, or terbium is available to inhibit corrosion. A tetravalent cerium, praseodymium, or terbium species that exhibits low solubility will not only fail to inhibit corrosion, but can promote localized crevice corrosion and result in enhanced corrosion rates. In order to form an effective conversion coating, the tetravalent cerium, praseodymium, or terbium compounds formed in the coating must be in a “sparingly soluble”
20 form. It is difficult to place specific solubility values to these optimum “sparingly soluble” coating materials because there appear to be several variables associated with what makes an optimum coating material. If the tetravalent cerium, praseodymium, or terbium is incorporated in the coating in the form of a tetravalent cerium, praseodymium, or terbium/valency stabilizer complex, which exhibits a solubility in water of between about 5×10^{-5} and about 5×10^{-2} moles
25 per liter of tetravalent cerium, praseodymium, or terbium, then appreciable corrosion inhibition will be observed. Coatings that incorporate stabilized tetravalent cerium, praseodymium, or terbium compounds that fall outside of this particular solubility range may also exhibit some corrosion inhibition. For example, compositions with solubilities as high as 5×10^{-1} moles per liter or as low as 1×10^{-5} moles per liter of tetravalent cerium, praseodymium, or terbium at
30 standard temperature and pressure, exhibited some corrosion resistance, although not as great as those compounds which fall within the optimum solubility range. The degree of effectiveness

will depend on the particular compound itself. The solubility characteristics of the tetravalent cerium, praseodymium, or terbium in the conversion coatings must be controlled through the use of stabilizer materials which form compounds that fall within a desired solubility range. In this way, a "controlled release" of tetravalent cerium, praseodymium, or terbium can be achieved,
5 much as a "timed release" of hexavalent chromium is achieved in the state-of-the-art systems.

4) The "valence stabilizer" helps establish an electrostatic barrier layer around the cation-stabilizer complex in aqueous solutions. The nature and character of the electrostatic double-layer surrounding the cation-stabilizer complex may be controlled and modified by careful
10 selection of stabilizer species. Characteristics such as the electrical dipole moment and the shape/conformation (for steric effects) of the stabilizer were found to influence the performance of the conversion coating. In general, the electrostatic double layer formed acts to protect the cation from premature reaction with hydronium, hydroxide, and other ions in solution. The formation of electrostatic barrier layers also helps to impede the passage of corrosive ions
15 through the conversion coatings to the metallic surface.

This phenomena is exhibited in the hexavalent chromium systems, wherein the highly charged hexavalent chromium is surrounded by very polar ferricyanide ions. The orientation of the dipoles of the ferricyanide ions with respect to the highly charged chromate ion serves to attract additional layers of ions in the aqueous solution. These ions form a protective shell
20 around the cation-stabilizer complex.

5) The coating material may also exhibit ion exchange behavior towards alkali species. This optional consideration is important for the formation of conversion coatings which resist corrosion because alkali ions (especially sodium) are notoriously corrosive towards alloys
25 which contain metals such as aluminum, magnesium, or zinc. The hexavalent chromium-ferricyanide complex formed in the conventional systems also exhibits this ion exchange phenomena.

The corrosion resistance of a number of aluminum alloys as tested using both ASTM B-117 and ASTM G-85 has been enhanced through the use of stabilized tetravalent cerium,
30 praseodymium, or terbium conversion coatings. Not only do these optimized coatings retard corrosion to a higher degree than other known tetravalent cerium baths, but their corrosion

resistance is comparable to that of hexavalent chromium systems. Unlike the prior art, the tetravalent cerium conversion coatings of the present invention do not result in the formation of cerium oxide or hydrated cerium oxide barrier layers with no active corrosion-inhibiting functionality.

5 The valence stabilizers can be inorganic or organic. A multitude of organic and inorganic stabilizer materials have been used.

In one aspect, the invention comprises a mechanistic and chemical approach to the production of corrosion-resistant conversion coatings using tetravalent cerium, praseodymium, or terbium. This approach uses stabilizer materials which form compounds with tetravalent cerium, praseodymium, or terbium that are sparingly soluble in aqueous solution, typically from about 5×10^{-2} to about 5×10^{-5} moles/liter of tetravalent ion. This solubility range provides a release of tetravalent cerium, praseodymium, or terbium at a rate sufficiently slow enough that protection will be provided for an extended period of time and fast enough to inhibit corrosion during conventional accelerated corrosion testing methods such as ASTM B-117 and ASTM G-85 for conversion coatings. Compounds that fall slightly outside of this solubility range (as high as 5×10^{-1} to as low as 1×10^{-5} moles/liter of tetravalent cerium, praseodymium, or terbium at standard temperature and pressure) may also prove to be effective conversion coatings under certain conditions. However, compounds that exhibit aqueous solubilities far outside of the target range are unlikely to be effective corrosion inhibitors. The solubility of the formed tetravalent cerium, praseodymium, or terbium compounds plays a significant role in the effectiveness of the formed coating. Solubility control can be achieved using organic or inorganic stabilizer materials.

In another aspect, the invention is the achievement of corrosion-resistant conversion coatings using tetravalent cerium, praseodymium, or terbium. This approach also utilizes stabilizer materials, which form compounds that exhibit dipoles so as to form electrostatic barrier layers composed of ions, such as hydronium (H_3O^+) or hydroxide (OH^-). The formation of these barrier layers through the use of stabilizer materials can be achieved using organic or inorganic materials.

In an optional aspect, the invention is the achievement of corrosion-resistant conversion coatings using tetravalent cerium, praseodymium, or terbium by the use of stabilizer materials,

which form compounds that exhibit ion exchange behavior towards alkali ions. The formation of this ion exchange behavior can be achieved through the use of organic or inorganic materials.

In another optional aspect, the invention is the achievement of corrosion-resistant conversion coatings using preparative agents in conjunction with the cerium, praseodymium, or terbium to strip uncontrolled native oxide layers on the work piece surface, as well as to control the rate of coating deposition. Typical preparative agents for the formation of tetravalent cerium, praseodymium, or terbium conversion coatings are fluorides and fluorine-containing chemicals. Acidic species or other halides such as chlorides, bromides, and iodides can be used, but are less effective than fluorides as preparative agents.

In another optional aspect, the invention is the achievement of superior corrosion-resistant conversion coatings by allowing the deposited tetravalent cerium-, praseodymium-, or terbium-containing coating to reach a desired thickness and/or morphology in order to maximize adhesion to the work piece, as well as maximizing adhesion of subsequently-applied paint films to the conversion coating. Ideally, the thickness of the formed tetravalent cerium, praseodymium, or terbium conversion coating should be approximately 200 nanometers. The minimum thickness allowable for a satisfactory pinhole-free tetravalent cerium, praseodymium, or terbium conversion coating is approximately 25 nanometers, and the maximum allowable thickness is approximately 10,000 nanometers. The morphology of the formed conversion coating should be sufficient to allow for paint films to adhere to it. A "mud crack" or "honeycomb" morphology is typical.

Accordingly, it is an object of the present invention to provide non-toxic corrosion-protection conversion coating baths based on tetravalent cerium, praseodymium, or terbium and methods of making and using the same. These and other objects and advantages of the present invention will be more fully understood from the following detailed description of the invention. It is noted that the scope of the claims is defined by the recitations therein and not by the specific discussion of features and advantages set forth in the present description.

DETAILED DESCRIPTION OF THE INVENTION

A) STARTING MATERIALS

Five general starting materials can be used for the conversion coating baths of the present invention. These include: a cerium, praseodymium, or terbium source; an oxidation source

(optional); a preparation agent source (optional); a valence stabilizer source; and additional solubility control agents (optional). These materials may be included as neat compounds in the conversion coating bath, or may be added to the conversion coating bath as already-prepared solutions. Further enhancements to the formed coating may be imparted through the use of 5 additional starting materials. Foremost among these are agents to improve the color-fastness of the coating.

1) Cerium, Praseodymium, or Terbium Source

a) Cerium Source

10 The cerium precursor compounds can be almost any cerium compound in which the cerium is in either the trivalent or tetravalent oxidation state. Water-soluble precursors are typically used. Examples of inorganic trivalent ("cerous") cerium precursor compounds include, but are not restricted to: cerous nitrate, cerous sulfate, cerous perchlorate, cerous chloride, cerous fluoride, cerous bromide, cerous iodide, cerous bromate, and complex fluorides such as cerous fluosilicate, cerous fluotitanate, cerous fluozirconate, cerous fluoborate, and cerous fluoaluminate. Organometallic trivalent cerium precursor compounds include, but are not limited to, cerous formate, cerous acetate, cerous propionate, cerous butyrate, cerous glycolate, cerous lactate, cerous sulfonate, cerous alkyl sulfonate, cerous alkoxysulfonate, cerous aromatic sulfonate, cerous aromatoxy sulfonate, cerous sulfamate, cerous alkyl phosphates, and cerous acetylacetone. Complex trivalent cerium precursor compounds include, but are not limited to, ammonium cerous sulfate, ammonium cerous nitrate, ammonium cerous oxalate, magnesium cerous nitrate, magnesium cerous sulfate, alkali cerous nitrate, and alkali cerous sulfate.

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25 The cerium precursor may also be a compound in which the cerium is already in the tetravalent ("ceric") oxidation state. Examples of these compounds include, but are not restricted to: ceric chloride, ceric fluoride, ceric perchlorate, ceric sulfate, ceric nitrate, ceric acetate, ceric propionate, ceric butyrate, ammonium ceric nitrate, ammonium ceric sulfate, magnesium ceric nitrate, magnesium ceric sulfate, alkali ceric nitrate, and alkali ceric sulfate.

30 Insoluble trivalent or tetravalent cerium compounds may be acceptable in some coating solutions, particularly if acids are used as the preparative agent. Examples of insoluble trivalent cerium compounds include cerous carbonate, cerous phosphate, cerous sulfide, cerous fluorocarbonate, cerous benzoate, cerous oxalate, cerous malonate, cerous tartrate, cerous malate,

cerous citrate, cerous thiocyanate, cerous salicylate, cerous oxide, and cerous hydroxide.

Examples of insoluble tetravalent cerium precursors are ceric hydroxide species (i.e., ceric hydroxysulfate, ceric hydroxychloride, ceric hydroxynitrate, ceric hydroxyphosphate, ceric hydroxyperchlorate, and ceric hydroxyacetate) with a hydroxide content of 50% or less.

5 It may not be necessary to add a separate cerium source for these conversion coating solutions if a cerium-containing alloy is to be treated. The preparative agent contained within these conversion coating formulations can dissolve some of the cerium in the substrate. This will result in trivalent cerium ions being present in the coating solution. A suitable oxidizer can then oxidize the trivalent cerium to the necessary tetravalent oxidation state during or after coating
10 deposition.

b) Praseodymium Source

The tetravalent praseodymium ion (Pr^{+4}) is an even better oxidizing species than Ce^{+4} . It has a radius of 0.085 nanometers, carries a charge of $+4$, and has a redox potential of approximately +3.2 V. However, it has a correspondingly lower stability both in and out of solution. Therefore, valence stabilization of this ion is needed in order to use it effectively in a conversion coating. The very large redox potential of Pr^{+4} makes it prone to rapid reduction, and few materials will effectively stabilize Pr^{+4} in a sparingly soluble complex, which make its routine application problematic. Tetravalent praseodymium can be made using chemical or
20 electrolytic oxidation, as can trivalent praseodymium.

Praseodymium precursors can be nearly any water soluble praseodymium compound in which the praseodymium has a trivalent or tetravalent oxidation state. Water-soluble precursors are typically used. Inorganic praseodymium precursor compounds include, but are not limited to, praseodymium nitrate, praseodymium sulfate, praseodymium perchlorate, praseodymium chloride, praseodymium fluoride, praseodymium bromide, praseodymium iodide, praseodymium bromate, and complex fluorides such as praseodymium fluosilicate, praseodymium fluotitanate, praseodymium fluozirconate, praseodymium fluoborate, and praseodymium fluoaluminate.

Organometallic praseodymium precursor compounds include, but are not limited to, praseodymium formate, praseodymium acetate, praseodymium propionate, praseodymium lactate, praseodymium benzenesulfonate, and praseodymium acetylacetone. Complex praseodymium precursor compounds include, but are not limited to, ammonium praseodymium

sulfate, ammonium praseodymium nitrate, magnesium praseodymium nitrate, magnesium praseodymium sulfate, alkali praseodymium nitrate, and alkali praseodymium sulfate.

c) Terbium Source

The tetravalent terbium ion (Tb^{+4}) is an even better oxidizing species than Ce^{+4} . It has a radius of 0.076 nanometers, carries a charge of $+4$, and has a redox potential of approximately +3.2 V. However, it has a correspondingly lower stability both in and out of solution. Therefore, valence stabilization of this ion is needed in order to use it effectively in a conversion coating. The very large redox potential of Tb^{+4} makes it prone to rapid reduction, and few materials will effectively stabilize Tb^{+4} in a sparingly soluble complex, which make its routine application problematic. Tetravalent terbium can be made using chemical or electrolytic oxidation, as can trivalent terbium.

Terbium precursors can be nearly any water soluble terbium compound in which the terbium has a trivalent or tetravalent oxidation state. Water-soluble precursors are typically used. Inorganic terbium precursor compounds include, but are not limited to, terbium nitrate, terbium sulfate, terbium perchlorate, terbium chloride, terbium fluoride, terbium bromide, terbium iodide, terbium bromate, and complex fluorides such as terbium fluosilicate, terbium fluotitanate, terbium fluozirconate, terbium fluoborate, and terbium fluoaluminate.

Organometallic terbium precursor compounds include, but are not limited to, terbium formate, terbium acetate, terbium propionate, terbium lactate, terbium benzenesulfonate, and terbium acetylacetone. Complex terbium precursor compounds include, but are not limited to, ammonium terbium sulfate, ammonium terbium nitrate, magnesium terbium nitrate, magnesium terbium sulfate, alkali terbium nitrate, and alkali terbium sulfate.

d) Mixed Cerium, Praseodymium, and Terbium Sources

It is also possible to use mixtures of cerium, praseodymium, and/or terbium sources as feedstock for material preparation. Inclusion of other rare earths (such as yttrium, lanthanum, or neodymium) that cannot be oxidized to the tetravalent state is also permissible. Additionally, minerals that serve as ores for rare earths are ideal source materials for this application. For example, sulfuric acid is often applied to rare earth ores to separate the rare earth mixtures (REM) from native rock. If these sulfuric acid extracts were in turn to be supplied with oxidizers

and valence stabilizers, source material for this application is achieved. Examples of rare earth-containing minerals suitable for this application are bastnaesite $[(\text{REM})\text{CO}_3\text{F}]$, monazite $[(\text{REM})\text{PO}_4]$, xenotime $[(\text{REM})\text{PO}_4]$, loparite $[(\text{REM}, \text{Na}, \text{Ca})(\text{Ti}, \text{Nb})\text{O}_3]$, lanthanite $[(\text{REM})_2(\text{CO}_3)_3]$, rhabdophane $[(\text{REM})\text{PO}_4]$, fergusonite $[(\text{REM})\text{NbO}_4]$, cebaite $[\text{Ba}_3(\text{REM})_2(\text{CO}_3)_5\text{F}_2]$, aeschynite $[(\text{Ca}, \text{REM})(\text{Ti}, \text{Nb})(\text{O}, \text{OH})_6]$, lucasite $[(\text{REM})\text{Ti}_2(\text{O}, \text{OH})_6]$, stillwellite $[(\text{REM}, \text{Ca})\text{BSiO}_5]$, samarskite $[(\text{REM}, \text{Fe})_3(\text{Nb}, \text{Ta}, \text{Ti})_5\text{O}_{16}]$, parisite $[\text{Ca}(\text{REM})_2(\text{CO}_3)_3\text{F}_2]$, gadoliniite $[\text{Be}_2\text{Fe}(\text{REM})_2\text{Si}_2\text{O}_{10}]$, fluocerite $[(\text{REM})\text{F}_3]$, cerianite $[(\text{REM})\text{O}_{2-3}]$, churchite $[(\text{REM})\text{PO}_4]$, or combinations thereof.

10 2) Oxidation Source

Oxidizers serve two important functions within the coating: 1) they act in cooperation with the stabilizer to impede the flow of ionic species through the coating, therefore minimizing charge transport, and 2) if a scratch is formed in the coating, these oxidizing species act to repair the breach by oxidizing the metal in the presence of water, and quickly reforming an oxide barrier. The effectiveness of the oxidizing species is a function of its individual oxidation-reduction potential, with more highly oxidized species exhibiting greater corrosion protection.

In order to provide adequate oxidation potential in the conversion coating solution, especially if trivalent cerium, praseodymium, or terbium compounds are utilized as precursors, an oxidizing species is also included as a starting material. Additional amounts of oxidizer may be added to help control and maintain a desired amount of Ce^{+4} in the conversion coating solution by reoxidizing Ce^{+4} that has been reduced. Because of the high potential of the redox reaction needed to oxidize trivalent cerium, praseodymium, or terbium to tetravalent cerium, praseodymium, or terbium, strong oxidizers must be utilized for this purpose. These oxidizers may be gaseous, liquid, or solid in form. Solid oxidizers are typically used for this application due to ease of handling and reagent measurement. Other starting materials (cerium, praseodymium, or terbium source, fluoride source, stabilizer source) will frequently also be solids. Liquid oxidizers may also be used, but handling and accurate process metering have proven difficult. Gaseous oxidizers may be the most cost effective and chemically efficient on a large scale, but are also the most problematic due to handling and venting concerns.

30 Examples of oxidizers suitable for the purpose of producing and maintaining the cerium, praseodymium, or terbium ions in the tetravalent charge state include, but are not restricted to:

peroxides and peroxy compounds (including superoxides, persulfates, perborates, pernitrates, perphosphates, percarbonates, persilicates, peraluminates, pertitanates, perzirconates, permolybdates, pertungstates, pervanadates, and organic peroxyacid derivatives), ozone, hypochlorites, chlorates, perchlorates, nitrates, nitrites, vanadates, iodates, hypobromites, 5 chlorites, bromates, permanganates, periodates, and dissolved oxygen. Both inorganic and organic derivatives of these compounds may be used. Typical oxidizers are peroxides, persulfates, perbenzoates, periodates, bromates, hypochlorites, and gaseous dissolved oxygen, including the oxygen content of air. In general, any inorganic, organic, or combination species that has an oxidation potential of +1.6 V or higher (at a pH of 1) will be capable of oxidizing 10 trivalent cerium to the tetravalent oxidation state. The formation of tetravalent praseodymium or terbium requires higher oxidation potentials. In the presence of suitable valence stabilizer compounds, tetravalent praseodymium or terbium can be formed from praseodymium or terbium solutions with an oxidation potential of +2.0 V or higher (at a pH of 1).

Oxidation of the cerium, praseodymium, or terbium to the tetravalent state may also be 15 achieved in the conversion coating solution through electrolytic means. In most instances, however, this approach may not be economically feasible due to the large energy costs associated with electrolytic oxidation. Chemical oxidation, such as that described above, currently offers the lowest-cost means to achieve oxidation of the cerium, praseodymium, or terbium to the tetravalent state.

It is also possible to deposit trivalent cerium, praseodymium, or terbium in a conversion 20 coating, and then apply a second solution containing an oxidizer to oxidize trivalent cerium, praseodymium, or terbium to tetravalent cerium, praseodymium, or terbium. This, however, is less typical because the percentage of deposited cerium, praseodymium, or terbium that will be in the tetravalent state will be less than if tetravalent cerium, praseodymium, or terbium were 25 deposited directly.

In many of the the conversion coating solutions based on hexavalent chromium, 30 oxidation sources are added to speed up the conversion coating process. Hence, they are termed “accelerators” in the hexavalent chromium formulations. Because the application of an acid (i.e., a conversion coating solution) to an electronegative metal will result in the formation of hydrogen gas, cathodic areas on the treated metal will be partially blocked from further coating formation. Oxidizers (“accelerators”) act to eliminate hydrogen gas formation, thereby

minimizing its barrier effect, and hence accelerating the overall deposition rate. It is for this reason that it is also desirable to have oxidizers in the initial conversion coating bath.

3) Preparative Agent Source

5 Uniform, adherent, low-defect film growth can be achieved if the conversion coat is deposited on a suitably prepared surface. Removing pre-existing “wild” native oxides is the first step to achieve the formation of high-quality conversion coatings. A preparative agent is any material that removes (dissolves and breaks up) preexisting surface oxides and provides a bare metal surface on which to deposit the conversion coating. The hexavalent chromium 10 formulations term these materials “activators” or “surface etchants.” The breakup and dissolution of the surface oxide in solution produces a bare unprotected metal suited for controlled oxidation, textures the surface, and encourages precipitation of the conversion coat compounds at the metal surface by locally raising the solution pH.

15 Fluoride acids and salts work especially well as preparative agents in conversion coating baths. The complex fluoride anions hexafluorozirconate (ZrF_6^{-2}) and hexafluorotitanate (TiF_6^{-2}) are superior fluoride sources for this application. Hexafluorosilicates (SiF_6^{-2}) can be used, but they result in a reduced level of subsequent corrosion protection. The potassium, lithium, sodium, and ammonium salts of these anions work especially well for this application, with potassium performing the best.

20 Other complex fluorides, including, but not restricted to, fluoroaluminates (e.g., AlF_6^{-3} or AlF_4^{-1}), fluoroborates (e.g., BF_4^{-1}), fluorogallates (e.g., GaF_4^{-1}) fluoroindates (e.g., InF_4^{-1}), fluorogermanates (e.g., GeF_6^{-2}), fluorostannates (e.g., SnF_6^{-2}), fluorophosphates (e.g., PF_6^{-1}), fluoroarsenates (e.g., AsF_6^{-1}), fluoroantimonates (e.g., SbF_6^{-1}), fluorobismuthates (e.g., BiF_6^{-1}), fluorosulfates (e.g., SF_6^{-2}), fluoroselenates (e.g., SeF_6^{-2}), fluorotellurates (e.g., TeF_6^{-2} or $TeOF_5^{-1}$), 25 fluorocuprates (e.g., CuF_3^{-1} or CuF_4^{-2}), fluoroargentates (e.g., AgF_3^{-1} or AgF_4^{-2}), fluorozincates (e.g., ZnF_4^{-2}), fluorohafnates (e.g., HfF_6^{-2}), fluorovanadates (e.g., VF_7^{-2}), fluoroniobates (e.g., NbF_7^{-2}), fluorotantalates (e.g., TaF_7^{-2}), fluoromolybdates (e.g., MoF_6^{-3}), fluorotungstates (e.g., WF_6^{-1}), fluoroyttrates (e.g., YF_6^{-3}), fluorolanthanates (e.g., LaF_6^{-3}), fluorocerates (e.g., CeF_6^{-3} or CeF_6^{-2}), fluoromanganates (e.g., MnF_6^{-2}), fluoroferrates (e.g., FeF_6^{-3}), fluoronickelates (e.g., 30 NiF_6^{-2}), and fluorocobaltates (e.g., CoF_6^{-2}) are also suitable fluoride sources, but these offer even

less corrosion protection than hexafluorosilicates. Water-soluble potassium, sodium, lithium, or ammonium salts of these anions are typical.

Simple inorganic fluorides such as potassium fluoride (KF), potassium hydrogen fluoride (KHF₂), sodium fluoride (NaF), sodium hydrogen fluoride (NaHF₂), lithium fluoride (LiF), lithium hydrogen fluoride (LiHF₂), ammonium fluoride (NH₄F), ammonium hydrogen fluoride (NH₄HF₂), and even hydrofluoric acid solutions (HF) can also be used as a fluoride source. By analogy, organic compounds that provide a ready supply of aqueous fluoride ions will likewise serve as adequate fluoride sources.

Other halide species, such as chlorides (Cl⁻), bromides (Br⁻), and iodides (I⁻) can also function as preparative agents, although their efficiency in stripping the surface oxide will not be as great as the fluorides. Inorganic or organic compounds that release chloride, bromide, or iodide anions can function as preparative agents, as can a number of complex chlorides and bromides that are similar to those described for the fluorides. By analogy, complex hexachlorozirconates (ZrCl₆⁻²), hexachlorotitanates (TiCl₆⁻²), and hexachlorosilicates (SiCl₆⁻²) should function better than other chloride sources, and analogous complex bromide and iodide sources will function better than other bromides and iodides.

Acidic species, such as nitric acid, sulfuric acid, phosphoric acid, pyrophosphoric acid, hydrochloric acid, perchloric acid, hydrobromic acid, hydriodic acid, iodic acid, periodic acid, disulfuric acid, selenic acid, telluric acid, polyphosphoric acid, cyclophosphoric acid, phytic acid, boric acid, carboxylic acids, phosphonic acids, and sulfonic acids can also function as preparative agents. Of these, nitric acid is the most useful as a preparative agent.

Acidic species based on metal salts that exhibit a pH below 7 when placed into solution can also be used as preparative agents. The advantage in the use of these species is that they can help eliminate the need for fluoride species as preparative agents, which are regulated in some locations. Metal salts of titanium, zirconium, niobium, tantalum, molybdenum, tungsten, vanadium, aluminum, silicon, tin, antimony, bismuth, tellurium, yttrium, and lanthanum are especially useful for this process. Halides, nitrates, sulfates, perchlorates, and carboxylates of these metals, including double salts with alkali metals or ammonium are most suited as acidic metal salts due to their water solubility.

Although it is less desirable, hydroxides can also function as preparative agents. For example, under high pH conditions zinc and aluminum are known to dissolve in water, through

the formation of zincate or aluminate anions. The use of hydroxides such as sodium, potassium, lithium, or ammonium derivatives will result in this pH rise.

Changes in the concentrations of the fluoride components also had significant effects upon the character of the deposited coating. It was found that the corrosion resistance of the formed coating was reduced if the fluoride concentration in solution came near or exceeded its solubility in water. Craters form in the coating, apparently caused by excess back etching of deposited oxides. The concentration of fluoride also appears to influence the thickness of the formed coating. The substrate metal remains bright and shiny at very low fluoride concentrations. These effects were found to begin when the ratio of fluoride ions to cerium, praseodymium, or terbium ions in the coating solution dropped below 0.05.

Fluoride species with different alkali metals appeared to have negligible effect upon the coating or its corrosion resistance. The use of lithium did not result in any improvement in corrosion resistance. Changes in the fluoride's associated alkali metals (e.g., K_2ZrF_6 , Na_2ZrF_6) did alter the solubility of fluoride in solution and so control the amount of fluoride available to etch the metal surface.

If a preparative agent is not included in the conversion coating bath, then the "wild" native oxides must be removed by some other process prior to the application of the conversion coating.

4) Valence Stabilizers

Corrosion resistance comparable to that of hexavalent chromium can be achieved by the use of valence stabilized tetravalent cerium, praseodymium, or terbium ions in the conversion coating solutions. Valence stabilization has not been recognized previously as an important consideration in the development of effective corrosion-inhibiting conversion coats. A variety of inorganic and organic stabilizers are available that can control such properties as solubility, mobility, ion exchange, and binder compatibility. The stabilizer complex can also act as an ion-exchange host and/or trap for alkali or halide ions in solution.

Cerium, praseodymium, and terbium are effective as oxidation corrosion inhibitors if they can be supplied in sufficient quantities in the tetravalent charge state when brought into contact with unprotected bare metal. The Ce^{+4} ionic radius of 0.087 nanometers is larger than the 0.044 nanometers of the hexavalent chromium ion, and so it will have a correspondingly

lower charge density (electrostatic field) per ion. The Pr⁺⁴ ionic radius of 0.085 nanometers and Tb⁺⁴ ionic radius of 0.076 nanometers are also larger than hexavalent chromium.

As noted in the Summary of the Invention, the valence stabilizer serves a number of important functions in the establishment of a successful conversion coating. First, the valence stabilizer, when used with tetravalent cerium, praseodymium, or terbium, results in a "sparingly soluble" Ce⁺⁴-, Pr⁺⁴-, or Tb⁺⁴-valence stabilizer complex. Although the exact solubility of this complex can be slightly modified through the incorporation of different cations or anions (either through the dissolution of the coated metal, or the subsequent treatment by additional solubility control agents), appreciable corrosion inhibition will be observed if the tetravalent cerium, praseodymium, or terbium is incorporated in the conversion coating as a Ce⁺⁴-, Pr⁺⁴-, or Tb⁺⁴-stabilizer complex that exhibits a solubility in water of between about 5×10^{-5} moles per liter and about 5×10^{-2} moles per liter of available Ce⁺⁴, Pr⁺⁴, or Tb⁺⁴. Therefore, any material (inorganic or organic) in the coating bath that complexes with tetravalent cerium, praseodymium, or terbium and results in the formation of a Ce⁺⁴-, Pr⁺⁴-, or Tb⁺⁴-containing complex, which exhibits solubilities within or near this solubility range, can serve as a valence stabilizer for tetravalent cerium, praseodymium, or terbium.

Conversion coatings which incorporate stabilized tetravalent cerium, praseodymium, or terbium compounds that fall outside this particular solubility range may exhibit some degree of corrosion inhibition and may be effective conversion coatings under certain circumstances.

Although not as effective as those compounds within the optimum solubility range, compositions with solubilities as high as 5×10^{-1} moles per liter or as low as 1×10^{-5} moles per liter of tetravalent cerium, praseodymium, or terbium, at standard temperature and pressure (about 25°C and about 760 Torr), exhibited some corrosion resistance. For example, in situations where the substrate metal pieces are exposed to environments which require much more immediate corrosion exposure (e.g., sudden immersion in seawater), adequate corrosion protection can be achieved through the formation of a tetravalent cerium, praseodymium, or terbium compound which exhibits a higher solubility in water (e.g., 5×10^{-1} to 5×10^{-3} moles/liter tetravalent cerium, praseodymium, or terbium). In this way, a more "immediate" release of protective tetravalent cerium, praseodymium, or terbium ions can be achieved, although the tetravalent cerium, praseodymium, or terbium will be depleted faster from the coating. Tetravalent cerium, praseodymium, or terbium solubilities that are lower than this optimum range (e.g., 1×10^{-5} to 1

x 10⁻³ moles/liter of tetravalent cerium, praseodymium, or terbium) may be desirable for some situations (e.g., in nearly pure water with low aeration rates). However, compounds that exhibit solubilities far outside the target range are unlikely to be effective corrosion inhibitors.

The solubility characteristics of the tetravalent cerium, praseodymium, or terbium in the conversion coatings is controlled with stabilizer materials that form compounds within the desired solubility range. The exact solubility will be strongly dependent on the application of the conversion coating and net aqueous solubility of overlying paints and coatings.

The formation of conversion coatings with the proper release rate of Ce⁺⁴, Pr⁺⁴, or Tb⁺⁴ ions is problematic because of the instability of Ce⁺⁴ and especially Pr⁺⁴ or Tb⁺⁴ out of solution. Tetravalent cerium compounds, such as ammonium ceric nitrate, and ammonium ceric sulfate are generally too soluble to serve as effective corrosion inhibitors if incorporated into a conversion coating. Oxides and hydroxides of Ce⁺⁴ are often too insoluble in water to serve effectively as corrosion inhibitors in a conversion coating. For example, ceric oxide (CeO₂) is so insoluble that its solubility has never been accurately determined. The more soluble “hydrated” ceric oxide [ceric hydroxide – Ce(OH)₄] is reported to exhibit a solubility product in water between 4.2 x 10⁻⁵¹ and 1.5 x 10⁻⁵¹, resulting in a cerium solubility of approximately 5 x 10⁻¹² moles/liter Ce⁺⁴ (see Tarayan, V. M. and Eliazyan, L. A., *Izvest. Akad. Nauk Armyan. S.S.R., Ser. Khim. Nauk* 10: 189-93, (1957) in *General and Physical Chemistry*, vol. 2, col. 9722 (1958) (Abstract)). Similarly, tetravalent praseodymium oxide (Pr₆O₁₁) is reported to exhibit solubility in water of 6.5 x 10⁻⁷ moles/liter Pr⁺⁴ (see Busch, W., *Z. anorg. allgem. Chem.* 161: 161-79 (1927) in *Chemical Abstracts*, vol. 21, p. 2412 (Abstract)). For these low solubility compounds, the release rates of Ce⁺⁴ or Pr⁺⁴ are too low to compare adequately to Cr⁺⁶ from the state-of-the-art coatings.

The solution to providing a useful source of tetravalent cerium, praseodymium, or terbium at a metal surface is the creation of a sparingly soluble compound in which the Ce⁺⁴, Pr⁺⁴, or Tb⁺⁴ ion is shielded from premature reduction during and after conversion coating formation. The assembly of a protective shell around the highly charged Ce⁺⁴, Pr⁺⁴, or Tb⁺⁴ and its associated oxygen and hydroxyl species can help control the rate at which the cerium, praseodymium, or terbium is reduced and its oxygen is released. Proper selection of materials for forming the protective shell will allow solubility tailoring of the entire assembly to its

intended application environment. Valence stabilizers are materials that, when assembled, modify the rate of reduction and the solubility of the Ce⁺⁴, Pr⁺⁴, or Tb⁺⁴ ions.

The electrostatic character of the complex should also be considered in creating a Ce⁺⁴, Pr⁺⁴, or Tb⁺⁴ stabilizer complex with optimal corrosion resistance. Valence stabilizers can also contribute to the development of a substantial electrostatic double layer. An electrostatic double layer of polar or charged species such as hydronium (H₃O⁺) or hydroxide (OH⁻) ions surrounding the stabilized cerium, praseodymium, or terbium complex will help control cerium, praseodymium, or terbium reduction and solubility and enhance the barrier properties of the conversion coating. Valence stabilizers which form sparingly soluble cerium, praseodymium, or terbium complexes with enhanced electrostatic double layers will maximize the corrosion-inhibiting character of the conversion coating.

The tetravalent cerium, praseodymium, or terbium ions are larger than the hexavalent chromium ion, with less charge density over the surface of the ion. Therefore, the valence stabilizers for Ce⁺⁴, Pr⁺⁴, or Tb⁺⁴ must be more efficient in the establishment of dipole moments than the valence stabilizers typically used for hexavalent chromium so that comparable corrosion resistance can be achieved in relation to the state-of-the-art Cr⁺⁶ compositions. Valence stabilizers which have a comparable dipole moment to the Cr⁺⁶ stabilizers, or which exhibit even less of a dipole moment than the Cr⁺⁶ stabilizers can also function as valence stabilizers, but the resultant corrosion resistance of the conversion coatings will, in all probability, be less than for the current commercial hexavalent chromium-based conversion coatings.

Large spheres of hydration around corrosion inhibitors can act as electrostatic and physical barriers to the passage of large corrosive ions such as Cl⁻ and SO₄⁻² through the coating to the metal surface. The size of the electrostatic double layer is a function of the electrostatic potential at the complex surface and is inversely proportional to the ionic strength of the surrounding solution. Compounds that can carry a charge, have a natural electrostatic dipole, or can have a dipole induced, will likely form an electrostatic double layer in aqueous solution. However, these compounds do not normally act as corrosion inhibitors because they have not been optimized for that purpose.

These facts are relevant when tetravalent cerium's propensity for attracting hydroxide species such as OH⁻ in solution is considered. While a tetravalent cerium ion surrounded solely by OH⁻ [i.e., Ce(OH)₄] may have a slight degree of aqueous solubility, the much lower charge

density (electrostatic field) that is exhibited by Ce⁺⁴ (coupled with the muting effect of the surrounding OH⁻ ions) implies that the electrostatic double layer formed around this assemblage will be small. If fewer hydroxide species surround the tetravalent cerium ion [i.e., Ce(OH)₂²⁺ or Ce(OH)³⁺], the electrostatic double layer around these ionic assemblages is increased, which will result in increased corrosion protection. Tetravalent cerium surrounded by no hydroxide species offers the highest degree of corrosion protection.

A simple laboratory experiment confirms this effect. If tetravalent cerium hydroxide [Ce(OH)₄] is placed into deionized water of pH 7, only a minor pH change will be observed, implying that the ionic attraction of this species for hydronium or hydroxide species is minimal. However, if icosahedral Ce(NO₃)₆²⁻ (note that this ion contains no hydroxide) is placed into deionized water of pH 7, a quite remarkable pH drop to -1 can be observed. The released tetravalent cerium ions will scavenge virtually all of the available OH⁻ ions in solution (possibly even degrading H₂O itself to obtain OH⁻), resulting in this dramatic pH drop.

These factors account for the lower corrosion performance of the hydrous oxides and hydroxides formed in many of the prior art references. Because the electrostatic double layers of hydrated cerium oxides and hydroxides are so small, their ability to impede the progress of corroding species is very low, even in the event that a minor concentration of these complexes become soluble. Unlike the other known corrosion-resistant components described in the art, which extol the formation of hydrous cerium oxides and hydroxides, this invention recognizes that these species result in lower corrosion performance in side-by-side tests. In fact, any oxo- or hydroxo- coordination greater than 50% on the tetravalent cerium ions (i.e., greater than Ce(OH)₂²⁺ or CeO²⁺) is objectionable. It is also for this reason that this invention does not promote the use of wide band hydroxide or oxide as valence stabilizers for tetravalent cerium.

Optionally, the incorporation of the valence stabilizer (inorganic or organic) should result in the formation of a Ce⁺⁴-, Pr⁺⁴-, or Tb⁺⁴-valence stabilizer compound which exhibits ion exchange behavior towards alkali ions. As noted in the Summary of the Invention, this is not a requirement of the Ce⁺⁴-, Pr⁺⁴-, or Tb⁺⁴-valence stabilizer complex, but it is a desirable characteristic for enhanced corrosion resistance. Some existing state-of-the-art chromium systems exhibit this phenomena, but conversion coating compounds that do not exhibit this phenomena have been successfully demonstrated to inhibit corrosive attack.

Rare earth coordination chemistry, which has been the subject of numerous scientific studies for almost 100 years, identifies chemical binding preferences, structure stability, and physical properties of the resulting compounds. Producing effective Ce⁺⁴-, Pr⁺⁴-, or Tb⁺⁴-valence stabilizer complexes requires understanding the electrostatic and structural influence of candidate species on the complex. Stabilizers can be designed that result in cerium, praseodymium, or terbium compounds with the necessary physical, electrical, and chemical properties to form corrosion inhibitors with this information. Property tailoring can also take place through selection of specific anions or cations bound to the Ce⁺⁴-, Pr⁺⁴-, or Tb⁺⁴-valence stabilizer coordination complex.

The functional anatomy of inorganic stabilizers is simple because of the limited number of atoms and structural arrangements involved in their formation. The anatomy of organic stabilizers is not as simple. An organically stabilized cerium, praseodymium, or terbium complex may have one or more organic ligands that may have one or more bonding sites that can interact with the Ce⁺⁴, Pr⁺⁴, or Tb⁺⁴ ion/oxide cluster. The bonding groups can be the same or different atoms or functional groups on an individual or a variety of ligands. An organic stabilizer ligand can be modified in an unlimited number of ways to tailor its physical behavior with respect to such properties as chemical reactivity, solubility, electrostatic and polar character, and functional behavior.

The stability of the Ce⁺⁴-, Pr⁺⁴-, or Tb⁺⁴-valence stabilizer complex is strongly influenced by the charge, polarity sign, and degree of polarizability of specific binding sites. Factors influencing compound stability include: 1) ion-pair interactions for charged ligands and Ce⁺⁴, Pr⁺⁴, or Tb⁺⁴, 2) ion-dipole and ion-induced dipole interactions for neutral ligands, 3) hydrogen bonding, and 4) the hard-soft acid-base (HSAB) rules convention of coordination chemistry. HSAB rules help identify functional groups on ligands that might be effective as binding sites. Optimum binding for organic valence stabilizers to Ce⁺⁴, Pr⁺⁴, or Tb⁺⁴ will involve ligands with hard bonding species such as those that contain oxygen or nitrogen. Certain coordination complexes of the soft bases sulfur or phosphorus are also effective for binding with Ce⁺⁴, Pr⁺⁴, or Tb⁺⁴. HSAB rules can also help identify groups that might provide a degree of polarization to the stabilizer because of their large dipole moments.

The nature of bonding between the Ce⁺⁴, Pr⁺⁴, or Tb⁺⁴ ion/oxide cluster and the stabilizer ligand can be altered by using a substituent group to modify the stabilizer. Specific interactions

between the ligand and Ce⁺⁴, Pr⁺⁴, or Tb⁺⁴ can be tailored by substituent group selection, coupled with altering the size or geometry of the complexing ligand. For example, some substituent groups have large dipole moments associated with them, which will increase the electrostatic barrier layers associated with the cerium/valence stabilizer complexes. These include: ketones (=C=O), thioketones (=C=S), amides (-C[=O]-NR₂), thioamides (-C[=S]-NR₂), nitriles or cyano groups (-CN), isocyanides (-NC), nitroso groups (-N=O), thionitroso groups (-N=S), nitro groups (-NO₂), azido groups (-N₃), cyanamide or cyanonitrene groups (=N-CN), cyanate groups (-O-CN), isocyanate groups (-N=C=O), thiocyanate groups (-S-CN), isothiocyanate groups (-N=C=S), nitrosamine groups (=N-N=O), thionitrosamine groups (=N-N=S), nitramine groups (=N-NO₂), thionitramine groups (=N-NS₂), carbonylnitrene groups (-CO-N), thiocabonylnitrene groups (-CS-N), sulfenyl halides (-S-X), sulfoxides (=S=O), sulfones (=S[=O]₂), sulfinyl groups (-N=S=O), thiosulfinyl groups (-N=S=S), sulfenyl thiocyanato groups (-S-S-CN), sulfenyl cyanato groups (-S-O-CN), sulfodiimine groups (=S[=NH]₂), sulfur dihaloimido groups (-N=S[=O]X₂), sulfur oxide dihaloimido groups (-N=S[=O]X₂), aminosulfur oxide trihalide groups (=N-S[=O]X₃), sulfonyl azide groups (-S[=O]₂N₃), sulfonyl thiocyanate groups (-S[=O]₂SCN), sulfonyl cyanate groups (-S[=O]₂OCN), sulfonyl cyanide groups (-S[=O]₂CN), halosulfonate groups (-S[=O]₂O⁻X), phosphonyl thiocyanate groups (-P[=O]OHSCN), phosphonyl cyanate groups (-P[=O]OHOCN), and phosphonyl cyanide groups (-P[=O]OHCN). The polarization of the Ce⁺⁴-, Pr⁺⁴-, or Tb⁺⁴-stabilizer can therefore be optimized via evaluation of the effect of ligand type and substituents. The influence of the Ce⁺⁴, Pr⁺⁴, or Tb⁺⁴ ion on the aqueous solution outside of, or external to, the valence stabilizer shell (or hydration sphere) may play an important role in the complexation properties of a given ligand. It will also control the diameter of the hydration shell around the Ce⁺⁴-, Pr⁺⁴-, or Tb⁺⁴-stabilizer complex.

The number of binding sites available on the complexing ligand is important to the resulting Ce⁺⁴-, Pr⁺⁴-, or Tb⁺⁴-stabilizer's properties. Several ligands are needed to stabilize Ce⁺⁴, Pr⁺⁴, or Tb⁺⁴ effectively if the chosen ligand has only one binding site. Six NO₃⁻ ligands are needed to icosahedrally coordinate Ce⁺⁴ in a hexanitratocerate(IV) complex because NO₃⁻ has only one binding site. Bulky ligands with only one binding site, like pyridine, can be sterically hindered from packing tightly around the ion, which will result in decreased complex stability. Conversely, macrocyclic organic and polymeric inorganic ligands may have many suitable binding sites. However, instability will result if a Ce⁺⁴, Pr⁺⁴, or Tb⁺⁴ ion is not

completely embraced by all of the multiple macromolecular bonding sites on the ligand. For example, if a macromolecule surrounding the Ce⁺⁴ ion has an insufficient number of binding sites available for charge balance, then the Ce⁺⁴-stabilizer complex will be much less stable than with a macromolecule that contains an adequate number of sites.

5 The physical geometry of the binding sites is important to the stability of the Ce⁺⁴-, Pr⁺⁴-, or Tb⁺⁴-stabilizer complex. The influence of site geometry becomes evident when the solvation shell of a Ce⁺⁴, Pr⁺⁴, or Tb⁺⁴ ion is replaced by the ligand donor atoms as when conversion coatings are formed. The number of available ligand binding sites should be at least equal to the standard coordination number of the Ce⁺⁴, Pr⁺⁴, or Tb⁺⁴ ion. The balance between solvation of 10 the ligand and Ce⁺⁴, Pr⁺⁴, or Tb⁺⁴ and their complexation where Ce⁺⁴, Pr⁺⁴, or Tb⁺⁴ is solvated by a specific ligand is important in maintaining stability. Ce⁺⁴-, Pr⁺⁴-, or Tb⁺⁴-ligand attraction increases with the number of available binding sites on the ligand. However, with an increasing number of binding sites, site-site repulsions will also increase, resulting in lower stability.

15 The Ce⁺⁴, Pr⁺⁴, and Tb⁺⁴ ions generally favor complexation in the icosahedral (coordination number 12) or octahedral (coordination number 6) arrangements. However, these ions will occasionally be found in a square antiprismatic, cubic, or complex arrangement. Valence stabilizers (and stabilizer combinations) should be selected with the goal of achieving 20 these coordinations.

Inorganic materials that tend to “polymerize” and form octahedra or icosahedra (or a combination thereof) around ions such as Ce⁺⁴, Pr⁺⁴, or Tb⁺⁴ are termed isopolyanions, and their resultant complexes with Ce⁺⁴, Pr⁺⁴, or Tb⁺⁴ are termed heteropolyanions or heteropolymetallates. This polymerization of the inorganic valence stabilizer species results in stacks of octahedra or icosahedra with central cavities which can accommodate at least one Ce⁺⁴, Pr⁺⁴, or Tb⁺⁴ ion, thereby stabilizing it.

25 Valence stabilizers and combinations of stabilizers can be manipulated by the selection of “shaping groups” and heteroatoms positioned at the binding site. Inorganic valence stabilizers are typically oxygen-containing coordination compounds. Saturated organic chains can form flexible ligands that wrap around Ce⁺⁴, Pr⁺⁴, or Tb⁺⁴ and can enhance its stability. Unsaturated organics typically have less freedom to bend and contort and are less likely to be able to wrap 30 around the Ce⁺⁴, Pr⁺⁴, or Tb⁺⁴ ion. The addition of substituents onto an organic ligand may further restrict its freedom to flex.

The actual size of the valence stabilizer complex situated around the Ce⁺⁴, Pr⁺⁴, or Tb⁺⁴ ion has an important role in solubility control. Solubility of the complex scales roughly with the inverse of its physical diameter. Ce⁺⁴, Pr⁺⁴, or Tb⁺⁴ and their layer of negatively charged hydroxyl ions is small and results in its high degree of aqueous solubility. The field strength of
5 the complex also scales with the inverse of its physical diameter. Large complexes with an optimal degree of solubility will not necessarily be ideal with respect to the size of the electrostatic double layer. The size of the ligand is therefore balanced against the desired electrical properties.

The addition (or subtraction) of functional groups on organic valence stabilizers can be
10 used to modify the solubility of the formed Ce⁺⁴, Pr⁺⁴, or Tb⁺⁴/valence stabilizer species. For example, the addition of sulfonated groups (-SO₃⁻) to organic valence stabilizers will significantly increase the solubility in water. Other substituent groups that will increase the solubility in water include: carboxyl groups (-CO₂⁻), hydroxyl groups (-OH), ester groups (-CO₃⁻), carbonyl groups (=C=O), amine groups (-NH₂), nitrosamine groups (=N-N=O),
15 carbonylnitrene groups (-CO-N), sulfoxide groups (=S=O), sulfone groups (=S[=O]₂), sulfinyl groups (-N=S=O), sulfodiimines (=S[=NH]₂), sulfonyl halide groups (-S[=O]₂X), sulfonamide groups (-S[=O]₂NH₂), monohalosulfonamide groups (-S[=O]₂NHX), dihalosulfonamide groups (-S[=O]₂MX₂), halosulfonate groups (-S[=O]₂O⁻X), halosulfonate amide groups (=N-S[=O]₂X), aminosulfonate groups (=N-S[=O]₂OH), iminodisulfonate groups (-N[SO₃⁻]₂), phosphonate groups (-PO₃⁻²), phosphonamide groups (-PO₂NH₂⁻), phosphondiamide groups (-PO[NH₂]₂), aminophosphonate groups (=N-PO₃⁻²), and iminodiphosphonate groups (-N[PO₃⁻²]₂). Conversely, the addition of nitro groups (-NO₂), perfluoroalkyl groups (-C_xF_{2x+1}), perchloroalkyl groups (-C_xCl_{2x+1}), nitramine groups (=N-NO₂), thioketone groups (=C=S), sulfenyl halide groups (-S-X), or sulfur dihaloimide groups (-N=SX₂) to organic valence stabilizers will decrease the solubility in water. In this way, the solubility characteristics of valence stabilizers can be tailored to meet specific needs.
25

The physical, chemical, and electrostatic requirements for the design of effective Ce⁺⁴-, Pr⁺⁴-, or Tb⁺⁴-stabilizer complexes results in lists of stabilizers that may be divided into wide band or narrow band stabilizer classes. The compounds listed here are general guides for the initial selection of a coordination compound and do not represent a complete or final list. New organic and inorganic compounds are continuously being developed, compound toxicity limits
30

can change, and some currently available compounds may have been overlooked. Tailoring substituent groups and the selection of cations or anions for charge balance can influence whether a particular Ce^{+4} -, Pr^{+4} -, or Tb^{+4} -stabilizer complex will have a wide band or narrow band character.

5 Valence stabilizers for tetravalent cerium, praseodymium, or terbium that embody the desirable characteristics of stabilizers as described above are typical when designing a conversion coating for maximum effectiveness. These “wide band” stabilizers result in the formation of compounds that provide significant corrosion resistance when used with tetravalent cerium, praseodymium, or terbium. “Narrow band” valence stabilizers result in satisfactory 10 conversion coatings only under limited applications. Wide band conversion coatings for general purpose applications and narrow band conversion coatings for specific uses have been identified and developed. In general, valence stabilizers that form cerium, praseodymium, or terbium complexes which exhibit the necessary physical properties of stability, solubility, and polarization may be achieved with both inorganic and organic valence stabilizers. Ion exchange 15 behavior can also be achieved with both inorganic and organic coordination compounds.

Because of the much higher oxidation-reduction potential associated with Pr^{+4} and Tb^{+4} , the choice of suitable valence stabilizers for these species is much more limited and will be dealt with in a separate section (4f). Sections 4a through 4e describe suitable stabilizers for Ce^{+4} .

20 4a) Wide Band Inorganic Valence Stabilizers for Ce^{+4}

Wide band inorganic stabilizers are formed around the Ce^{+4} ion by polymerizing in the conversion coating solution near the metal surface being treated. Acidic coating solutions can become basic near the metal surface where precipitation of the cerium-stabilizer complex occurs during the coating process. Inorganic wide band valence stabilizers for Ce^{+4} include, but are not 25 limited to: molybdates (Mo^{+6} , Mo^{+5} , or Mo^{+4} , for example $[\text{Ce}^{+4}\text{Mo}_{12}\text{O}_{42}]^{8-}$, $[\text{Ce}^{+4}\text{Mo}_7\text{O}_{24}]^{2-}$, and $[\text{Ce}^{+4}_2\text{Mo}_{14}\text{O}_{48}]^{4-}$); tungstates (W^{+6} , W^{+5} , or W^{+4} , for example $[\text{Ce}^{+4}\text{W}_{12}\text{O}_{42}]^{8-}$, $[\text{Ce}^{+4}\text{W}_8\text{O}_{28}]^{4-}$, and $[\text{Ce}^{+4}\text{W}_{10}\text{O}_{35}]^{6-}$); vanadates (V^{+5} or V^{+4} , for example $[\text{Ce}^{+4}\text{V}_{18}\text{O}_{51}]^{8-}$); niobates (Nb^{+5} or Nb^{+4} , 30 for example $[\text{Ce}^{+4}\text{Nb}_2\text{O}_6(\text{OH})_4]^{2-}$); tantalates (Ta^{+5} or Ta^{+4} , for example $[\text{Ce}^{+4}\text{Ta}_2\text{O}_6(\text{OH})_4]^{2-}$); tellurates (Te^{+6} or Te^{+4} , for example $\text{Ce}^{+4}(\text{TeO}_4)_2$); periodates (I^{+7} , for example $[\text{Ce}^{+4}\text{IO}_6]^{1-}$); iodates (I^{+5} , for example $\text{Ce}^{+4}(\text{IO}_3)_4$); carbonates (C^{+4} , for example $[\text{Ce}^{+4}(\text{CO}_3)_5]^{6-}$); antimonates (Sb^{+5} or Sb^{+3}); stannates (Sn^{+4}); phosphates (P^{+5} , for example $\text{Ce}^{+4}_3(\text{PO}_4)_4$, $\text{Ce}^{+4}(\text{HPO}_4)_2$,

Ce⁺⁴P₂O₇, and [Ce⁺⁴(P₂O₇)₂]⁴⁻); nitrates (N⁺⁵, for example [Ce⁺⁴(NO₃)₆]²⁻); bromates (Br⁺⁵, for example Ce⁺⁴(BrO₃)₄); and sulfates (S⁺⁶, for example [Ce⁺⁴(SO₄)₄]⁴⁻). Many of these inorganics form octahedral or icosahedral heteropolytungstate structures on precipitation from solution. For example, tellurate ions begin to polymerize in solution near pH 5 and will complex with Ce⁺⁴ ions near the metal substrate as solution pH increases. The exact chemical nature of these valence stabilizers (i.e., chemical formulation and valence state of the atom in the center of the 5 icosahedra or octahedra) is highly dependent upon the specific pH and redox conditions:

The stability of the heteropolytungstates is a function of composition and structure. The relatively unstable Ce⁺⁴ ion is protected and stabilized within the surrounding octahedral or 10 icosahedral groups, although specific configurations of the heteropolytungstate anions differ from stabilizer to stabilizer (i.e., from molybdate to periodate to carbonate).

The dimensions of the octahedra and icosahedra are controlled by the size of the 15 heteroatom (e.g., Mo, W, Te) around which they are assembled. A Ce⁺⁴ ion trapped by the precipitation of these heteropolytungstates and its resulting "ion within a cage" structure can exhibit an even greater apparent volume due to the development of a large electrostatic double layer. This will influence both the valence stabilization of the Ce⁺⁴ as well as the solubility of the assembled complex. These compounds are also reported to be excellent ion exchange agents for alkali ions.

This caging structure serves to lower the solubility of the Ce⁺⁴ because the chemical 20 elements typically associated with these valence stabilizers (e.g., I, Te, Mo, W) are often inherently less soluble in water than Ce⁺⁴. These materials can also establish oriented dipoles with the interior Ce⁺⁴ ion, thereby forming the desired barrier layers (e.g., of hydronium ions), much as ferricyanide or molybdate probably contributes to the hexavalent chromium systems. Finally, the elements associated with these valence stabilizers themselves can contain high 25 valence ions, such as V⁺⁵, Te⁺⁶, or Mo⁺⁶, which will also serve somewhat in corrosion protection, although not to the degree of Ce⁺⁴, due to their lower redox potential.

Water-soluble precursors for the formation of these valence stabilizers are desirable in 30 order to ensure that sufficient material is available for coating deposition from aqueous solutions. Identification of suitable water-soluble precursors may be difficult, since many of the elements associated with these valence stabilizers (e.g., Mo, W, Te, etc.) do not typically form water-

soluble compounds (hence their beneficial use as a valence stabilizer). Representative examples of suitable precursors for “wide band” inorganic valence stabilizers are listed in Table 6.

The solubilities given in Table 6 are usually for the simplest salts of each compound.

More complex, partially “polymerized” salts for each compound (e.g., para- or meta-polymorphs) can also be used as precursors, although these polymorphs typically exhibit slightly lower solubilities in water than the simple salts. Peroxo-salts of these compounds, especially percarbonates, permolybdates, pertungstates, pertitanates, and pervanadates can also be utilized as precursors. Formation of the chosen heteropolytungstate from precursors such as the fluorides, chlorides, bromides, nitrates, and perchlorates (e.g., SnCl_4 to form heterostannates, and SbF_5 to form heteroantimonates) proved to be difficult, but may be acceptable under certain circumstances.

Ce^{+4} stabilized with a heteropolytungstate complex is an example of a wide band inorganically stabilized cerium complex. This complex is very stable and provides significant corrosion protection when it is used as a conversion coating. The size of the cavity developed at the center of a ligand with three or more bonding sites is important. A cavity that is too large or too small will tend to be less stable and less effective in use as a corrosion inhibitor.

The valence stabilizer can be a cross between two or more of the wide-band inorganic valence stabilizers listed above. For example, in some instances it may be desirable to form a valence stabilizer out of a periodate and a molybdate. During the coating process, both of these materials will polymerize to form a mixed periodate/molybdate valence stabilizer out of the conversion coating solution.

4b) Wide Band Organic Valence Stabilizers for Ce^{+4}

A variety of organic compounds meet the criteria to be typical valence stabilizers for Ce^{+4} . These coordination ligands produce Ce^{+4} valence stabilized complexes which fulfill the general requirements of a Ce^{+4} conversion coating material. Organic compounds can be very effective cerium stabilizers and provide the greatest degree of freedom in designing new stabilizer species with new functionalities. There are many more possible organic valence stabilizer species than inorganic valence stabilizers because of the large number of organic compounds and functionalities which exist. Some of the typical organic valence stabilizer species are listed in Table 1 below.

The number of wide band (and narrow band) organic compounds that are acceptable as valence stabilizers for tetravalent cerium is limited. Common organic compounds such as alcohols, aldehydes, ketones, esters, ethers, alkyl or aromatic halides, most carboxylic acids, anhydrides, phenols, sulfonic acids, phosphonic acids, carbohydrates, waxes, fats, sugars, and oils are not as effective as the structural types described in the Tables herein to stabilize the tetravalent cerium ion. At best, some of the organic types described in these Tables may presently be used for other industrial applications, but their incorporation into corrosion-inhibiting blends to stabilize tetravalent cerium has heretofore been unrecognized.

The choice of substituent functional groups on these general classes of valence stabilizers will affect the physicochemical properties of the Ce⁺⁴-containing complex and the corrosion resistance achieved using that complex. For example, the addition of -NH₂, or =O substituents increases the net polarization of the overall Ce⁺⁴-valence stabilizer complex, but this will also increase its water solubility. Careful molecular design of Ce⁺⁴ complexes is necessary to achieve desired performance characteristics.

In general, the bonding atoms in typical organic valence stabilizers are oxygen or nitrogen, with sulfur or phosphorus being acceptable in some circumstances. Sulfur or phosphorus are complexed with Ce⁺⁴ most frequently in association with oxygen. Bonding atoms such as carbon, silicon, tin, arsenic, selenium, and antimony are much less desirable due to problems with valence stability, toxicity, or solubility. These valence stabilizers all serve to stabilize the Ce⁺⁴ ion within a sparingly soluble complex that can exhibit a polar character in aqueous solution.

Table 1. Wide Band Organic Valence Stabilizers for the Ce⁺⁴ Ion

General Structural Name (Type of Organic)	Structural Representation
<u>N Valence Stabilizer #1:</u> Monoamines (N Monodentates)	NH ₃ , NH ₂ R, NHR ₂ , and NR ₃ where R represents H or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N Valence Stabilizer #2:</u> Diamines (N-N Bidentates)	R'-N-R-N-R'', where R, R', and R'' represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N Valence Stabilizer #3:</u> Triamines (either N-N Bidentates or N-N Tridentates)	R-N-R'-N-R''-N-R''', where R, R', R'', and R''' represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N Valence Stabilizer #4:</u> Tetramines (N-N Bidentates, N-N Tridentates, or N-N Tetradentates)	R-N-R'-N-R''-N-R'''-N-R'''', where R, R', R'', R''', and R''''' represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N Valence Stabilizer #5:</u> Pentamines (N-N Bidentates, N-N Tridentates, or N-N Tetradentates)	R-N-R'-N-R''-N-R'''-N-R''''-N-R''''', where R, R', R'', R''', R''''', and R''''' represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.

<u>N Valence Stabilizer #6:</u> Hexamines (N-N Bidentates, N-N Tridentates, N-N Tetridentates, or N-N Hexadentates)	R-N-R'-N-R"-N-R'''-N-R"""-N-R""", where R, R', R", R"', R''', R''""", and R''"" represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N Valence Stabilizer #7:</u> Five-Membered Heterocyclic Rings containing One, Two, Three, or Four Nitrogen Atoms wherein at least one Nitrogen Atom is a Binding Site (N Monodentates or N-N Bidentates)	Five membered heterocyclic ring containing one, two, three, or four nitrogen atoms, all of which may or may not function as binding sites. Can include other ring systems bound to this heterocyclic ring, but they do not coordinate with the stabilized, high valence metal ion. Ring can also contain O, S, or P atoms. This 5-membered ring and/or attached, uncoordinating rings may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>N Valence Stabilizer #8:</u> Six-Membered Heterocyclic Rings containing One, Two, Three, or Four Nitrogen Atoms wherein at least one Nitrogen Atom is a Binding Site (N Monodentates or N-N Bidentates)	Six membered heterocyclic ring containing one, two, three, or four nitrogen atoms, all of which may or may not function as binding sites. Can include other ring systems bound to this heterocyclic ring, but they do not coordinate with the stabilized, high valence metal ion. Ring can also contain O, S, or P atoms. This 6-membered ring and/or attached, uncoordinating rings may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>N Valence Stabilizer #9:</u> Five-Membered Heterocyclic Rings containing One, Two, Three, or Four Nitrogen Atoms and having at least one additional Nitrogen Atom Binding Site not in a Ring (N Monodentates, N-N Bidentates, N Tridentates, N-N Tetridentates, or N-N Hexadentates)	Five membered heterocyclic ring(s) containing one, two, three, or four nitrogen atoms. In addition, ligand contains additional nitrogen-containing substituents (usually amines) that constitute N binding sites. Can include other ring systems bound to the heterocyclic ring or to the N-containing substituent, but they do not coordinate with the stabilized, high valence metal ion. Ring(s) can also contain O, S, or P atoms. This 5-membered ring(s) and/or attached, uncoordinating rings and/or N-containing substituent(s) may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>N Valence Stabilizer #10:</u> Six-Membered Heterocyclic Rings	Six membered heterocyclic ring(s) containing one, two, three, or four nitrogen atoms. In

<p>containing One, Two, Three, or Four Nitrogen Atoms at least one additional Nitrogen Atom Binding Site not in a Ring (N Monodentates, N-N Bidentates, N-N Tridentates, N-N Tetridentates, or N-N Hexadentates)</p>	<p>addition, ligand contains additional nitrogen-containing substituents (usually amines) that constitute N binding sites. Can include other ring systems bound to the heterocyclic ring or to the N-containing substituent, but they do not coordinate with the stabilized, high valence metal ion. Ring(s) can also contain O, S, or P atoms. This 6-membered ring(s) and/or attached, uncoordinating rings and/or N-containing substituent(s) may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.</p>
<p><u>N Valence Stabilizer #11:</u> Five-Membered Heterocyclic Rings containing One, Two, Three, or Four Nitrogen Atoms at least one additional Nitrogen Atom Binding Site in a Separate Ring (N Monodentates, N-N Bidentates, N-N Tridentates, N-N Tetridentates)</p>	<p>Five membered heterocyclic ring(s) containing one, two, three, or four nitrogen atoms. In addition, ligand contains additional nitrogen-containing rings that constitute N binding sites. Can include other ring systems bound to the N-containing heterocyclic rings, but they do not coordinate with the stabilized, high valence metal ion. Ring(s) can also contain O, S, or P atoms. This 5-membered ring(s) and/or additional N-containing ring(s) and/or attached, uncoordinating rings may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.</p>
<p><u>N Valence Stabilizer #12:</u> Six-Membered Heterocyclic Rings containing One, Two, Three, or Four Nitrogen Atoms at least one additional Nitrogen Atom Binding Site in a Separate Ring (N Monodentates, N-N Bidentates, N-N Tridentates, N-N Tetridentates)</p>	<p>Six membered heterocyclic ring(s) containing one, two, three, or four nitrogen atoms. In addition, ligand contains additional nitrogen-containing rings that constitute N binding sites. Can include other ring systems bound to the N-containing heterocyclic rings, but they do not coordinate with the stabilized, high valence metal ion. Ring(s) can also contain O, S, or P atoms. This 6-membered ring(s) and/or additional N-containing ring(s) and/or attached, uncoordinating rings may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.</p>
<p><u>N Valence Stabilizer #13:</u> Two-, Three-, Four-, Six-, Eight-, and Ten-Membered Macrocyclics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Nitrogen (usually amine or imine groups) and are not contained in</p>	<p>Macrocyclic ligands containing two, three, four, six, eight, or ten nitrogen binding sites to valence stabilize the central metal ion. Can include other hydrocarbon or ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbons/rings may or may</p>

Component Heterocyclic Rings (N-N Bidentates, N-N Tridentates, N-N Tetridentates, and N-N Hexadentates)	not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>N Valence Stabilizer #14:</u> Four-, Six-, Eight-, or Ten-Membered Macrocyclics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Nitrogen and are contained in Component 5-Membered Heterocyclic Rings (N-N Bidentates, N-N Tridentates, N-N Tetridentates, or N-N Hexadentates)	Macroyclic ligands containing a total of four, six, eight, or ten five-membered heterocyclic rings containing nitrogen binding sites. Can include other hydrocarbon/ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbon/rings may or may not have halogen or polarizing or water-insolubilizing groups attached.
<u>N Valence Stabilizer #15:</u> Four-, Six-, Eight-, or Ten-Membered Macrocyclics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Nitrogen and are contained in a Combination of 5-Membered Heterocyclic Rings and Amine or Imine Groups (N-N Bidentates, N-N Tridentates, N-N Tetridentates, or N-N Hexadentates)	Macroyclic ligands containing at least one 5-membered heterocyclic ring. These heterocyclic rings provide nitrogen binding sites to valence stabilize the central metal ion. Other amine or imine binding sites can also be included in the macrocyclic ligand, so long as the total number of binding sites is four, six, eight, or ten. Can include other hydrocarbon/ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbon/rings may or may not have halogen or polarizing or water-insolubilizing groups attached.
<u>N Valence Stabilizer #16:</u> Four-, Six-, Eight-, or Ten-Membered Macrocyclics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Nitrogen and are contained in Component 6-Membered Heterocyclic Rings (N-N Bidentates, N-N Tridentates, N-N Tetridentates, or N-N Hexadentates)	Macroyclic ligands containing a total of four, six, eight, or ten six-membered heterocyclic rings containing nitrogen binding sites. Can include other hydrocarbon/ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbon/rings may or may not have halogen or polarizing or water-insolubilizing groups attached.
<u>N Valence Stabilizer #17:</u> Four-, Six-, Eight-, or Ten-Membered Macrocyclics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Nitrogen and are contained in a Combination of 6-Membered Heterocyclic	Macroyclic ligands containing at least one 6-membered heterocyclic ring. These heterocyclic rings provide nitrogen binding sites to valence stabilize the central metal ion. Other amine or imine binding sites can also be included in the macrocyclic ligand, so long as the total number of binding sites is four, six, eight, or ten. Can include other

Rings and Amine or Imine Groups (N-N Bidentates, N-N Tridentates, N-N Tetridentates, or N-N Hexadentates)	hydrocarbon/ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbon/rings may or may not have halogen or polarizing or water-insolubilizing groups attached.
<u>N Valence Stabilizer #18:</u> Amidines and Diamidines (N-N Bidentates and N-N Tetridentates)	R'-NH-C(-R)=N-R'', where R, R', and R'' represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N Valence Stabilizer #19:</u> Biguanides (Imidodicarbonimidic Diamides or Dihydrazides), Biguanidines, Imidotricarbonimidic Diamides or Dihydrazides, Imidotetraacarbonimidic Diamides or Dihydrazides, Dibiguanides, Bis(biguanidines), Polybiguanides, and Poly(biguanidines) (N-N Bidentates, N-N Tridentates, N-N Tetridentates, and N-N Hexadentates)	RR'-N-C(=NH)-NR''-C(=NH)-NR'''R'''' for biguanides, RR'-N-C(=NH)-NR''-NH-C(=NH)-NR'''R'''' for biguanidines, where R, R', R'', R''', and R'''' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N Valence Stabilizer #20:</u> Diamidinomethanes, Bis(amidinomethanes), and Poly(amidinomethanes) (N-N Bidentates, N-N Tridentates, N-N Tetridentates, and N-N Hexadentates)	RR'-N-C(=NH)-CR''R''''-C(=NH)-NR''''R''''', where R, R', R'', R''', R''''', and R''''' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N Valence Stabilizer #21:</u> Imidoylguanidines, Amidinoguanidines, Bis(imidoylguanidines), Bis(amidinoguanidines), Poly(imidoylguanidines), and Poly(amidinoguanidines) (N-N Bidentates, N-N Tridentates, N-N Tetridentates)	RR'-N-C(=NH)-NR''-C(=NH)-R''' for imidoylguanidines, and RR'-N-C(=NH)-NR''-NH-C(=NH)-R''' for amidinoguanidines, where R, R', R'', and R''' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N Valence Stabilizer #22:</u> Diformamidine oxides (Dicarbonimidic Diamides or Dihydrazides), Tricarbonimidic Diamides or Dihydrazides,	RR'-N-C(=NH)-O-C(=NH)-NR''R''', where R, R', R'', and R''' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally

Tetracarbonimidic Diamides or Dihydrazides, Bis(diformamidine oxides), and Poly(diformamidine oxides) (N-N Bidentates, N-N Tridentates, N-N Tetridentates)	having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N Valence Stabilizer #23:</u> Diformamidine Sulfides (Thiodicarbonimidic Diamides or Dihydrazides), Thiotricarbonimidic Diamides or Dihydrazides, Thiotetracarbonimidic Diamides or Dihydrazides, Bis(diformamidine sulfides), and Poly(diformamidine sulfides) (N-N Bidentates, N-N Tridentates, N-N Tetridentates)	RR'-N-C(=NH)-S-C(=NH)-NR''R'''', where R, R', R'', and R''' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N Valence Stabilizer #24:</u> Imidodicarbonimidic Acids, Diimidodicarbonimidic Acids, Imidotricarbonimidic Acids, Imidotetracarbonimidic Acids, and derivatives thereof (N-N Bidentates, N-N Tridentates, N-N Tetridentates, and N-N Hexadentates)	R-O-C(=NH)-NR'-C(=NH)-O-R'' for imidodicarbomimidic acids, and R-O-C(=NH)-NR'-NH-C(=NH)-O-R'' for diimidodicarbonimidic acids, where R, R', and R'' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N Valence Stabilizer #25:</u> Thioimidodicarbonimidic Acids, Thiodiimidodicarbonimidic Acids, Thioimidotricarbonimidic Acids, Thioimidotetracarbonimidic Acids, and derivatives thereof (N-N Bidentates, N-N Tridentates, N-N Tetridentates, and N-N Hexadentates)	R-S-C(=NH)-NR'-C(=NH)-S-R'' for thioimidodicarbonimidic acids, and R-S-C(=NH)-NR'-NH-C(=NH)-S-R'' for thiodiimidodicarbonimidic acids, where R, R', and R'' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N Valence Stabilizer #26:</u> Diimidoylimines, Diimidoylhydrazides, Bis(diimidoylimines), Bis(diimidoylhydrazides), Poly(diimidoylimines), and Poly(diimidoylhydrazides) (N-N Tridentates and N-N Hexadentates)	R-C(=NH)-NR'-C(=NH)-R'' for diimidoylimines, and R-C(=NH)-NR'-NH-C(=NH)-R'' for diimidoylhydrazides, where R, R', and R'' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.

	P atoms.
<u>N Valence Stabilizer #27:</u> Imidosulfamides, Diimidosulfamides, Bis(imidosulfamides), Bis(diimidosulfamides), Poly(imidosulfamides), and Poly(diimidosulfamides) (N-N Bidentates, N-N Tridentates, N-N Tetridentates, and N-N Hexadentates)	RR'-N-S(=NH)(=O)-OR" or RR'-N-S(=NH)(=O)-N-R'R'" for imidosulfamides, and RR'-N-S(=NH)(=NH)-OR" or RR'-N-S(=NH)(=NH)-N-R'R'" for diimidosulfamides, where R, R', R", and R"" represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N Valence Stabilizer #28:</u> Phosphoramidimidic Triamides, Bis(phosphoramidimidic triamides), and Poly(phosphoramidimidic triamides) and derivatives thereof (N-N Bidentates, N-N Tridentates, N-N Tetridentates, and N-N Hexadentates)	(NH=)P(-NRR')(-NR''R'')(-NR'''R'''), where R, R', R'', R''', and R'''' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N Valence Stabilizer #29:</u> Phosphoramidimidic Acid, Phosphorodiamidimidic Acid, Bis(Phosphoramidimidic Acid), Bis(Phosphorodiamidimidic Acid), Poly(Phosphoramidimidic Acid), Poly(Phosphorodiamidimidic Acid), and derivatives thereof (N-N Bidentates, N-N Tridentates, N-N Tetridentates, and N-N Hexadentates)	(NH=)P(-NRR')(OH) ₂ for phosphoramidimidic acid, and (NH=)P(-NRR')(-NR''R'')(OH) for phosphorodiamidimidic acid, where R, R', R'', and R''' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N Valence Stabilizer #30:</u> Phosphoramidimidodithioic Acid, Phosphorodiamidimidodithioic Acid, Bis(Phosphoramidimidodithioic Acid), Bis(Phosphorodiamidimidodithioic Acid), Poly(Phosphoramidimidodithioic Acid), Poly(Phosphorodiamidimidodithioic Acid), and derivatives thereof (N-N Bidentates, N-N Tridentates, N-N Tetridentates, and N-N Hexadentates)	(NH=)P(-NRR')(SH) ₂ for phosphoramidimidodithioic acid, and (NH=)P(-NRR')(-NR''R'')(SH) for phosphorodiamidimidodithioic acid, where R, R', R'', and R''' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N Valence Stabilizer #31:</u> Azo compounds including triazenes with amino, imino, oximo, diazeno, or hydrazido substitution at the ortho- (for aryl) or alpha- or beta- (for alkyl) positions, Bis[o-(H ₂ N-)]	R-N=N-R' for azo compounds, R-N=N-NH-R' for triazenes, where R, and R' represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or

<p>or alpha- or beta-(H₂N-)azo compounds], or Poly[o-(H₂N-) or alpha- or beta-(H₂N-)azo compounds) (N-N Bidentates, N-N Tridentates, N-N Tetridentates, or N-N Hexadentates)</p>	<p>water-insolubilizing/solubilizing groups attached. (Must include ortho-amino, imino, oximo, diazeno, or hydrazido substituted aryl azo compounds, and alpha- or beta-amino, imino, oximo, diazeno, or hydrazido alkyl azo compounds.) Ligand can also contain nonbinding N, O, S, or P atoms.</p>
<p><u>N Valence Stabilizer #32:</u> Diazeneformimidamides (Diazeneamidines), Diazeneacetimidamides (Diazene-alpha-amidinoalkanes(alkenes)), Bis(diazeneformimidamides), Bis(diazeneacetimidamides), Poly(diazeneformimidamides), and Poly(diazeneacetimidamides) (N-N Bidentates, N-N Tetridentates, and N-N Hexadentates)</p>	<p>R-N=N-C(=NH)-NR'R" for diazeneformimidamides, and R-N=N-CR'R"-C(=NH)-NR""R"" for diazeneacetimidamides, where R, R', R", R"", and R"" represent H, NH₂, or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.</p>
<p><u>N Valence Stabilizer #33:</u> Diazeneformimidic Acid, Diazeneacetimidic Acid, Bis(diazeneformimidic acid), Bis(diazeneacetimidic acid), Poly(diazeneformimidic acid), Poly(diazeneacetimidic acid), and derivatives thereof (N-N Bidentates, N-N Tetridentates, and N-N Hexadentates)</p>	<p>R-N=N-C(=NH)-OR' for diazeneformimidic acid, and R-N=N-CR'R"-C(=NH)-OR"" for diazeneacetimidic acid, where R, R', R", and R"" represent H, NH₂, or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.</p>
<p><u>N Valence Stabilizer #34:</u> Diazeneformimidothioic Acid, Diazeneacetimidothioic Acid, Bis(diazeneformimidothioic acid), Bis(diazeneacetimidothioic acid), Poly(diazeneformimidothioic acid), Poly(diazeneacetimidothioic acid), and derivatives thereof (N-N Bidentates, N-N Tetridentates, and N-N Hexadentates)</p>	<p>R-N=N-C(=NH)-SR' for diazeneformimidothioic acid, and R-N=N-CR'R"-C(=NH)-SR"" for diazeneacetimidothioic acid, where R, R', R", and R"" represent H, NH₂, or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.</p>
<p><u>N Valence Stabilizer #35:</u> Imidoyl diazenes, Bis(imidoyl diazenes), and Poly(imidoyl diazenes), (N-N Bidentates, N-N Tetridentates and N-N Hexadentates)</p>	<p>R-N=N-C(=NH)-R' or R-N=N-CR'R"-C(=NH)-R""", where R, R', R", and R"" represent H, NH₂, or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or</p>

	P atoms.
<u>N Valence Stabilizer #36:</u> Diazenediformimidamides (1,2-Diazenediamidines), Diazenediacetimidamides (1,2-Diazene-di-alpha-amidinoalkanes(alkenes)), Bis(diazenediformimidamides), Bis(diazenediacetimidamides), Poly(diazenediformimidamides), and Poly(diazenediacetimidamides) (N-N Tridentates and N-N Hexadentates)	RR'-N-C(=NH)-N=N-C(=NH)-NR''R''' for diazenediformimidamides, and RR'-N-C(=NH)-CR''R'''-N=N-CR''''R'''''-C(=NH)-NR''''''R''''''' for diazenediacetimidamides, where R, R', R'', R''', R''''', R'''''''', and R''''''' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N Valence Stabilizer #37:</u> Diazenediformimidic Acid, Diazenediacetimidic Acid, Bis(diazenediformimidic acid), Bis(diazenediacetimidic acid), Poly(diazenediformimidic acid), and Poly(diazenediacetimidic acid), and derivatives thereof (N-N Tridentates and N-N Hexadentates)	RO-C(=NH)-N=N-C(=NH)-OR' for diazenediformimidic acid, and RO-C(=NH)-CR'R''-N=N-CR''''R'''''-C(=NH)-OR'''''' for diazenediacetimidic acid, where R, R', R'', R''', R''''', and R''''''' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N Valence Stabilizer #38:</u> Diazenediformimidothioic Acid, Diazenediacetimidothioic Acid, Bis(diazenediformimidothioic acid), Bis(diazenediacetimidothioic acid), Poly(diazenediformimidothioic acid), and Poly(diazenediacetimidothioic acid), and derivatives thereof (N-N Tridentates and N-N Hexadentates)	RS-C(=NH)-N=N-C(=NH)-SR' for diazenediformimidothioic acid, and RS-C(=NH)-CR'R''-N=N-CR''''R'''''-C(=NH)-SR'''''' for diazenediacetimidothioic acid, where R, R', R'', R''', R''''', and R''''''' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N Valence Stabilizer #39:</u> Diimidoyldiazenes, Bis(diimidoyldiazenes), and Poly(diimidoyldiazenes), (N-N Tridentates and N-N Hexadentates)	R-C(=NH)-N=N-C(=NH)-R'' or R-C(=NH)-CR'R''-N=N-CR''''R'''''-C(=NH)-R'''''', where R, R', R'', R''', R''''', and R''''''' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N Valence Stabilizer #40:</u> Ortho-amino (or -hydrazido) Substituted Formazans, Bis(o-amino or -hydrazido	R-N=N-CR'=N-NR''R''', where R, R', R'', and R''' represent H, or any organic functional group wherein the number of carbon atoms

<p>substituted formazans), and Poly(o-amino or -hydrazido substituted formazans) (N-N Bidentates, N-N Tridentates, N-N Tetridentates, and N-N Hexadentates)</p>	<p>ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. (Must include ortho-amine or hydrazide substituted aryl R derivatives, and beta-amine or hydrazide substituted alkyl R derivatives.) Ligand can also contain nonbinding N, O, S, or P atoms.</p>
<p><u>N Valence Stabilizer #41:</u> Ortho-amino (or -hydrazido) Substituted Azines (including ketazines), Bis(o-amino or hydrazido substituted azines), and Poly(o-amino or hydrazido substituted azines) (N-N Bidentates, N-N Tridentates, N-N Tetridentates, and N-N Hexadentates)</p>	<p>$RR'C=N-N=CR''R'''$ or $RR'C=N-NR''R'''$ (for ketazines), where R, R', R'', and R''' represent H, or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. (Must include ortho-amine or hydrazide substituted aryl R derivatives, and beta-amine or hydrazide substituted alkyl R derivatives.) Ligand can also contain nonbinding N, O, S, or P atoms.</p>
<p><u>N Valence Stabilizer #42:</u> Schiff Bases with one Imine (C=N) Group and with ortho- or alpha- or beta-amino or imino or oximo or diazeno or hydrazido substitution (N-N Bidentates, N-N Tridentates, N-N Tetridentates, N-N Pentadentates, or N-N Hexadentates). Also includes hydrazones with ortho-N substitution.</p>	<p>$RR'C=N-R''$, where R, R', and R'' represent H, or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. (Must contain ortho- or alpha- or beta-amino or imino or oximo or diazeno or hydrazido substitution.) Ligand can also contain nonbinding N, O, S, or P atoms.</p>
<p><u>N Valence Stabilizer #43:</u> Schiff Bases with two Imine (C=N) Groups and without ortho- (for aryl constituents) or alpha- or beta- (for alkyl constituents) hydroxy, carboxy, carbonyl, thiol, mercapto, thiocarbonyl, amino, imino, oximo, diazeno, or hydrazido substitution (N-N Bidentates). Also includes dihydrazones.</p>	<p>$RR'C=N-R''-N=CR''R'''$ or $R-N=C-R'-C=N-R'$ or $RC=N-R'-N=CR''$, where R, R', R'', R''', and R''' represent H, or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. (Not including ortho-, alpha-, or beta-hydroxy, carboxy, carbonyl, thiol, mercapto, thiocarbonyl, amino, imino, oximo, diazeno, or hydrazido substitution.) Ligand can also contain nonbinding N, O, S, or P atoms.</p>
<p><u>N Valence Stabilizer #44:</u> Schiff Bases with two Imine (C=N) Groups and with ortho- or alpha- or beta-amino or imino or oximo or diazeno or hydrazido substitution (N-N Tridentates, N-N Tetridentates, N-N Pentadentates, or N-N</p>	<p>$RR'C=N-R''-N=CR''R'''$ or $R-N=C-R'-C=N-R'$ or $RC=N-R'-N=CR''$, where R, R', R'', R''', and R''' represent H, or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-</p>

<p>Hexadentates). Also includes hydrazones with ortho-N substitution.</p>	<p>insolubilizing/solubilizing groups attached. (Must contain ortho- or alpha- or beta-amino or imino or oximo or diazeno or hydrazido substitution.) Ligand can also contain nonbinding N, O, S, or P atoms.</p>
<p><u>N Valence Stabilizer #45:</u> Schiff Bases with three Imine (C=N) Groups and without ortho- (for aryl constituents) or alpha- or beta- (for alkyl constituents) hydroxy, carboxy, carbonyl, thiol, mercapto, thiocarbonyl, amino, imino, oximo, diazeno, or hydrazido substitution (N-N Tridentates). Also includes trihydrazones.</p>	<p>$N(-R-N=CR'R'')_3$, where R, R', and R'' represent H, or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. (Not including ortho-, alpha-, or beta-hydroxy, carboxy, carbonyl, thiol, mercapto, thiocarbonyl, amino, imino, oximo, diazeno, or hydrazido substitution.) Ligand can also contain nonbinding N, O, S, or P atoms.</p>
<p><u>N Valence Stabilizer #46:</u> Schiff Bases with three Imine (C=N) Groups and with ortho- or alpha- or beta-amino or imino or oximo or diazeno or hydrazido substitution (N-N Tetridentates, N-N Pentadentates, or N-N Hexadentates)</p>	<p>$N(-R-N=CR'R'')_3$, where R, R', and R'' represent H, or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. (Must contain ortho- or alpha- or beta-amino or imino or oximo or diazeno or hydrazido substitution.) Ligand can also contain nonbinding N, O, S, or P atoms.</p>
<p><u>S Valence Stabilizer #1:</u> Macrocyclic, Macrobicyclic, and Macropolycyclic Oligothioketones (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Thioketones (typically in the beta position) (S-S Bidentates, S-S Tetridentates, and S-S Hexadentates)</p>	<p>Macrocyclic ligands containing two, four, or six thioketone binding sites to valence stabilize the central metal ion. Can include other hydrocarbon or ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbons/rings may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.</p>
<p><u>S Valence Stabilizer #2:</u> Macrocyclic, Macrobicyclic, and Macropolycyclic Dithiolenes (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of alpha, alpha dithiols (meaning two thiol groups on a single carbon atom in the ring) (S-S Bidentates, S-S Tetridentates, and S-S Hexadentates)</p>	<p>Macrocyclic ligands containing two, four, six, or eight 1,1-dithiolene binding sites to valence stabilize the central metal ion. Can include other hydrocarbon or ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbons/rings may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.</p>
<p><u>S Valence Stabilizer #3:</u> Dithioimidodialdehydes,</p>	<p>$RC(=S)-NR'-C(=S)-R''$ for dithioimidodialdehydes, and $RC(=S)-NR'-NH-$</p>

Dithiohydrazidodialdehydes (thioacyl thiohydrazides), Bis(dithioimidodialdehydes), Bis(dithiohydrazidodialdehydes), Poly(dithioimidodialdehydes), and Poly(dithiohydrazidodialdehydes) (S-S Bidentates, S-S Tridentates, S-S Tetridentates)	C(=S)-R" for dithiohydrazidodialdehydes (thioacyl thiohydrazides), where R, R', and R" represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S Valence Stabilizer #4:</u> Dithioimidodicarbonic acids, Dithiohydrazidodicarbonic acids, Bis(dithioimidodicarbonic acids), Bis(dithiohydrazidodicarbonic acids), Poly(dithioimidodicarbonic acids), Poly(dithiohydrazidodicarbonic acids) and derivatives thereof (S-S Bidentates, S-S Tridentates, S-S Tetridentates)	R-O-C(=S)-NR'-C(=S)-O-R" or R-S-C(=S)-NR'-C(=S)-S-R" for dithioimidodicarbonic acids, and R-O-C(=S)-NR'-NH-C(=S)-O-R" or R-S-C(=S)-NR'-NH-C(=S)-S-R" for dithiohydrazidodicarbonic acids, where R, R', and R" represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S Valence Stabilizer #5:</u> 1,3-Dithioketones (Dithio-beta-ketonates), 1,3,5-Trithioketones, Bis(1,3-Dithioketones), and Poly(1,3-Dithioketones) (S-S Bidentates, S-S Tridentates, S-S Tetridentates)	R-C(=S)-CR'R"-C(=S)-R'" where R, R', R", and R"" represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S Valence Stabilizer #6:</u> 1,2-Dithioketones (Dithiolenes, Dithio-alpha-ketonates), 1,2,3-Trithioketones, Dithiotropolonates, ortho-Dithioquinones, Bis(1,2-Dithioketones), and Poly(1,2-Dithioketones) (S-S Bidentates, S-S Tridentates, S-S Tetridentates)	R-C(=S)-C(=S)-R' where R and R' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S Valence Stabilizer #7:</u> Dithiomalonamides (Dithiomalonodiamides), Bis(dithiomalonamides), and Polydithiomalonamides (S-S Bidentates, S-S Tridentates, S-S Tetridentates)	RR'-N-C(=S)-CR''R'''-C(=S)-N-R''''R''''' where R, R', R'', R''', R''''', and R''''' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S Valence Stabilizer #8:</u> 2-Thioacetylthioacetamides, Bis(2-	RR'-N-C(=S)-CR''R'''-C(=S)-R'''' where R, R', R'', R''', and R''''' represent H, NH ₂ , or any

thioacylthioacetamides), and Poly(2-thioacylthioacetamides) (S-S Bidentates, S-S Tridentates, S-S Tetridentates)	organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S Valence Stabilizer #9:</u> Dithioacyl sulfides, Bis(dithioacyl sulfides), and Poly(dithioacyl sulfides) (S-S Bidentates, S-S Tridentates, S-S Tetridentates)	R-C(=S)-S-C(=S)-R' where R and R' represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S Valence Stabilizer #10:</u> Trithiodicarbonic Diamides, Bis(trithiodicarbonic diamides), and Poly(trithiodicarbonic diamides) (S-S Bidentates, S-S Tridentates, S-S Tetridentates)	RR'-N-C(=S)-S-C(=S)-N-R''R''' where R, R', R'', and R''' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S Valence Stabilizer #11:</u> Pentathio-, Tetraethio-, or Trithiodicarbonic Acids, Bis(pentathio-, tetrathio-, or trithiodicarbonic acids), Poly(pentathio-, tetrathio-, or trithiodicarbonic acids), and derivatives thereof (S-S Bidentates, S-S Tridentates, S-S Tetridentates)	R-S-C(=S)-S-C(=S)-S-R' for pentathiodicarbonic acids, R-O-C(=S)-S-C(=S)-S-R' for tetrathiodicarbonic acids, and R-O-C(=S)-S-C(=S)-O-R' for pentathiodicarbonic acids, where R and R' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S Valence Stabilizer #12:</u> Dithiohypophosphoric Acids, Bis(dithiohypophosphoric acids), and Poly(dithiohypophosphoric acids), and derivatives thereof (S-S Bidentates, S-S Tridentates, S-S Tetridentates)	(R-O-)(R'-O-)P(=S)-P(=S)(-O-R')(-O-R'''); (R-O-)(R'-S-)P(=S)-P(=S)(-S-R')(-O-R'''); or (R-S-)(R'-S-)P(=S)-P(=S)(-S-R')(-S-R'''), where R, R', R'', and R''' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms. Note: these ligands are not to be confused with hypophosphorous acid derivatives (hypophosphites) (R-O-R''R'''P(=O) which are very reducing and therefore unacceptable for stabilization of high valence states in metal ions.

<u>S Valence Stabilizer #13:</u> Dithiohypophosphoramides, Bis(dithiohypophosphoramides), and Poly(dithiohypophosphoramides) (S-S Bidentates, S-S Tridentates, S-S Tetridentates)	(RR'-N-)(R"R'"-N-)P(=S)-P(=S)(-N- R'"'R'"')(-N-R'"'"R'"'"'), where R, R', R", R"', R'"', R'"'', R'"''', and R'"'''' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms. Note: these ligands are not to be confused with hypophosphorous acid derivatives (hypophosphites) (R-O-)R"R'"P(=O) which are very reducing and therefore unacceptable for stabilization of high valence states in metal ions.
<u>S Valence Stabilizer #14:</u> Dithioimidodiphosphoric Acids, Dithiohydrazidodiphosphoric Acids, Bis(dithioimidodiphosphoric Acids), Bis(dithiohydrazidodiphosphoric Acids), Poly(dithioimidodiphosphoric Acids), Poly(dithiohydrazidodiphosphoric Acids), and derivatives thereof (S-S Bidentates, S-S Tridentates, S-S Tetridentates)	(R-O-)(R'-O-)P(=S)-NH-P(=S)(-O-R")(-O- R'"'); (R-O-)(R'-S-)P(=S)-NH-P(=S)(-S-R")(-O- R'"'); or (R-S-)(R'-S-)P(=S)-NH-P(=S)(-S-R")(- S-R'"') for dithioimidodiphosphoric acids, and – NH-NH- derivatives for dithiohydrazidodiphosphoric acids, where R, R', R", and R''' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water- insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S Valence Stabilizer #15:</u> Dithioimidodiphosphoramides, Dithiohydrazidodiphosphoramides, Bis(dithioimidodiphosphoramides), Bis(dithiohydrazidodiphosphoramides), Poly(dithioimidodiphosphoramides), and Poly(dithiohydrazidodiphosphoramides) (S-S Bidentates, S-S Tridentates, S-S Tetridentates)	(RR'-N-)(R"R'"-N-)P(=S)-NH-P(=S)(-N- R'"'R'"')(-N-R'"'"R'"'"') for dithioimidodiphosphoramides, and (RR'-N- (R"R'"-N-)P(=S)-NH-NH-P(=S)(-N- R'"'R'"')(-N-R'"'"R'"'"') for dithiohydrazidodiphosphoramides, where R, R', R", R'', R''', R''''', R'''''', and R'''''' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S Valence Stabilizer #16:</u> Dithiodiphosphoramides, Bis(dithioiphosphoramides), and Poly(dithiodiphosphoramides) (S-S Bidentates, S-S Tridentates, S-S	(RR'-N-)(R"R'"-N-)P(=S)-S-P(=S)(-N- R'"'R'"')(-N-R'"'"R'"'"'), or (RR'-N-)(R"R'"- N-)P(=S)-O-P(=S)(-N-R'"'R'"')(-N- R'"'"R'"'"'), where R, R', R", R''', R''''', R'''''', and R'''''' represent H, NH ₂ or any

Tetradentates)	organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S Valence Stabilizer #17:</u> Dithiodiphosphoric Acids, Bis(dithioiphosphoric Acids), Poly(dithiodiphosphoric Acids), and derivatives thereof (S-S Bidentates, S-S Tridentates, S-S Tetradentates)	(R-O-)(R'-O-)P(=S)-O-P(=S)(-O-R'')(-O-R'''); (R-O-)(R'-O-)P(=S)-S-P(=S)(-O-R'')(-O-R'''); (R-O-)(R'-S-)P(=S)-O-P(=S)(-S-R'')(-O-R'''); (R-O-)(R'-S-)P(=S)-S-P(=S)(-S-R'')(-O-R'''); or (R-S-)(R'-S-)P(=S)-S-P(=S)(-S-R'')(-S-R'''), where R, R', R'', R''', R'''', R''''', and R'''''' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water- insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S Valence Stabilizer #18:</u> Tri thiophosphoric Acids (Phosphorotri thioic Acids), Bis(tri thiophosphoric acids), Poly(tri thiophosphoric acids), and derivatives thereof (S-S Bidentates, S-S Tridentates, S-S Tetradentates)	(O=)P(-S-R)(-S-R')(-S-R'') or (S=)P(-S-R)(-S-R')(-O-R''), where R, R', and R'' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S Valence Stabilizer #19:</u> Dithiophosphoric Acids (Phosphorodithioic Acids), Bis(dithiophosphoric acids), Poly(dithiophosphoric acids), and derivatives thereof (S-S Bidentates, S-S Tridentates, S-S Tetradentates)	(O=)P(-S-R)(-S-R')(-O-R'') or (S=)P(-S-R)(-O-R')(-O-R''), where R, R', and R'' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S Valence Stabilizer #20:</u> Tetrathiophosphoric Acids (Phosphorotetrathioic Acids), Bis(tetrathiophosphoric acids), Poly(tetrathiophosphoric acids), and derivatives thereof (S-S Bidentates, S-S Tridentates, S-S Tetradentates)	(S=)P(-S-R)(-S-R')(-S-R''), where R, R', and R'' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water- insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S Valence Stabilizer #21:</u> Phosphoro(dithioperoxo)dithioic Acids, Bis[phosphoro(dithioperoxo)dithioic	(O=)P(-S-S-R)(-S-R')(-S-R'') or (S=)P(-S-S-R)(-S-R')(-O-R''), where R, R', and R'' represent H, NH ₂ or any organic functional

<p>Acids], Poly[phosphoro(dithioperoxo)dithioic Acids], and derivatives thereof (S-S Bidentates, S-S Tridentates, S-S Tetradentates)</p>	<p>group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.</p>
<p>S Valence Stabilizer #22: Phosphoro(dithioperoxo)thioic Acids, Bis[phosphoro(dithioperoxo)thioic Acids], Poly[phosphoro(dithioperoxo)thioic Acids], and derivatives thereof (S-S Bidentates, S-S Tridentates, S-S Tetradentates)</p>	<p>(O=)P(-S-S-R)(-S-R')(-O-R'') or (S=)P(-S-S-R)(-O-R')(-O-R''), where R, R', and R'' represent H, NH₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.</p>
<p>S Valence Stabilizer #23: Phosphoro(dithioperoxo)trithioic Acids, Bis[phosphoro(dithioperoxo)trithioic Acids], Poly[phosphoro(dithioperoxo)trithioic Acids], and derivatives thereof (S-S Bidentates, S-S Tridentates, S-S Tetradentates)</p>	<p>(S=)P(-S-S-R)(-S-R')(-S-R''), where R, R', and R'' represent H, NH₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.</p>
<p>S Valence Stabilizer #24: Beta-Mercaptothioketones, Beta-Mercaptothioaldehydes, Bis(beta-mercaptopthioketones), Bis(beta-mercaptopthioaldehydes), Poly(beta-mercaptopthioketones), and Poly(beta-mercaptopthioaldehydes) (S-S Bidentates, S-S Tridentates, S-S Tetradentates)</p>	<p>R-CR'(-SH)-CH₂-C(=S)-R'', where R, R', and R'' represent H, NH₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.</p>
<p>S Valence Stabilizer #25: N-(Aminomethylthiol)thioureas [N-(Aminomercaptomethyl)thioureas], Bis[N-(aminomethylthiol)thioureas], and Poly[N-(aminomethylthiol)thioureas] (S-S Bidentates, S-S Tridentates, S-S Tetradentates)</p>	<p>RR'-N-CH(-SH)-NR''-C(=S)-NR'''R''', where R, R', R'', R''', and R'''' represent H, NH₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.</p>
<p>S Valence Stabilizer #26: Dithioxamides, Bis(dithioxamides), and Poly(dithioxamides) (S-S Bidentates, S-S Tridentates, S-S Tetradentates)</p>	<p>RR'-N-C(=S)-C(=S)-N-R''R''', where R, R', R'', and R''' represent H, NH₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.</p>

	P atoms.
<u>S Valence Stabilizer #27:</u> 1,1-Dithiolates, Bis(1,1-dithiolates), and Poly(1,1-dithiolates) (S-S Bidentates and S-S Tetridentates)	RR'-C=C(-S)(-S'), where R and R' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S Valence Stabilizer #28:</u> Dithiomonocarboxylic Acids, Tri- and Tetrathiodicarboxylic Acids, Bis(dithiomonocarboxylic Acids), Bis(tri- and tetrathiodicarboxylic acids), Poly(dithiomonocarboxylic acids), Poly(tri- and tetrathiodicarboxylic acids), and derivatives thereof (S-S Bidentates and S-S Tetridentates)	R-C(=S)(-S-R') for dithiomonocarboxylic acids, and (R-S-)(S=)C-R'-C(=S)(-S-R'') for tri- and tetrathiodicarboxylic acids, where R, R', and R'' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S Valence Stabilizer #29:</u> Perthiomonocarboxylic Acids, Perthiodicarboxylic Acids, Bis(perthiomonocarboxylic acids), Bis(perthiodicarboxylic acids), Poly(perthiomonocarboxylic acids), Poly(perthiodicarboxylic acids), and derivatives thereof (S-S Bidentates and S-S Tetridentates)	R-C(=S)(-S-S-R') for perthiomonocarboxylic acids, and (R-S-S-)(S=)C-R'-C(=S)(-S-S-R'') for perthiodicarboxylic acids, where R, R', and R'' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S Valence Stabilizer #30:</u> Dithiocarbonates, Trithiocarbonates, Perthiocarbonates, Bis(dithiocarbonates), Bis(trithiocarbonates), and Bis(perthiocarbonates) (S-S Bidentates and S-S Tetridentates)	R-S-C(=S)-O-R' or R-S-C(=O)-S-R' for dithiocarbonates, R-S-C(=S)-S-R' for trithiocarbonates, and R-S-S-C(=S)-S-R' for perthiocarbonates, where R, and R' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S Valence Stabilizer #31:</u> Dithiocarbamates, Bis(dithiocarbamates), and Poly(dithiocarbamates) (including N-hydroxydithiocarbamates and N-mercaptodithiocarbamates) (S-S Bidentates, S-S Tridentates, and S-S Tetridentates)	RR'N ⁺ =C(SH)(SH), where R and R' represent H, OH, SH, OR'' (R'' = C ₁ -C ₃₀ alkyl or aryl), SR'' (R'' = C ₁ -C ₃₀ alkyl or aryl), NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or

	P atoms.
<u>S Valence Stabilizer #32:</u> Dithiocarbazates (Dithiocarbazides), Bis(dithiocarbazates), and Poly(dithiocarbazates) (S-S Bidentates, S-S Tridentates, and S-S Tetridentates; or possibly N-S Bidentates, N-S Tridentates, and N-S Tetridentates)	RR'N-NR"-C(=S)(SH), where R and R' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S Valence Stabilizer #33:</u> Thiocyanate ligands (S Monodentates)	Thiocyanates bound directly to the high valence metal ion.
<u>O Valence Stabilizer #1:</u> Biurets (Imidodicarbonic Diamides), Isobiurets, Biureas, Triurets, Triureas, Bis(biurets), Bis(isobiurets), Bis(biureas), Poly(biurets), Poly(isobiurets), and Poly(biureas) (O-O Bidentates, O-O Tridentates, O-O Tetridentates)	RR'-N-C(=O)-NR"-C(=O)-NR'''R"" for biurets, and RR'-N-C(=O)-NR"-NH-C(=O)-NR'''R"" for biureas, where R, R', R", R"', and R"" represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>O Valence Stabilizer #2:</u> Acylureas, Aroylureas, Bis(acylureas), Bis(aroylureas), Poly(acylureas), and Poly(aroylureas) (O-O Bidentates, O-O Tridentates, O-O Tetridentates)	RR'-N-C(=O)-NR"-C(=O)-R"" where R, R', R", and R"" represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>O Valence Stabilizer #3:</u> Imidodialdehydes, Hydrazidodialdehydes (Acyl hydrazides), Bis(imidodialdehydes), Bis(hydrazidodialdehydes), Poly(imidodialdehydes), and Poly(hydrazidodialdehydes) (O-O Bidentates, O-O Tridentates, O-O Tetridentates)	RC(=O)-NR'-C(=O)-R" for imidodialdehydes, and RC(=O)-NR'-NH-C(=O)-R" for hydrazidodialdehydes (acyl hydrazides), where R, R', and R" represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>O Valence Stabilizer #4:</u> Imidodicarbonic acids, Hydrazidodicarbonic acids, Bis(imidodicarbonic acids), Bis(hydrazidodicarbonic acids), Poly(imidodicarbonic acids), and Poly(hydrazidodicarbonic acids)	R-O-C(=O)-NR'-C(=O)-O-R" for imidodicarbonic acids, and R-O-C(=O)-NR'-NH-C(=O)-O-R" for hydrazidodicarbonic acids, where R, R', and R" represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-

derivatives thereof (O-O Bidentates, O-O Tridentates, O-O Tetridentates)	insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>O Valence Stabilizer #5:</u> Imidodisulfamic Acid, Imidodisulfuric Acid, Bis(Imidodisulfamic Acid), Bis(Imidodisulfuric Acid), Poly(Imidodisulfamic Acid), and Poly(Imidodisulfuric Acid) and derivatives thereof (O-O Bidentates, O-O Tridentates, O-O Tetridentates)	RR'-N-S(=O)(=O)-NR''-S(=O)(=O)-NR'''R'''' for imidodisulfamic acid, and R-O-S(=O)(=O)-NR'-S(=O)(=O)-OR'' for imidosulfuric acid, where R, R', and R'' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>O Valence Stabilizer #6:</u> 1,3-Diketones (Beta-Diketonates), 1,3,5-Triketones, Bis(1,3-Diketones), and Poly(1,3-Diketones), all with a Molecular Weight Greater than 125 (O-O Bidentates, O-O Tridentates, O-O Tetridentates)	R-C(=O)-CR'R''-C(=O)-R''' where R, R', R'', and R''' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms. If these ligands exhibit a molecular weight less than or equal to 125, the solubility of the resultant diketone complex will be too high.
<u>O Valence Stabilizer #7:</u> 1,2-Diketones (Alpha-Diketonates), 1,2,3-Triketones, Tropolonates, ortho-Quinones, Bis(1,2-Diketones), and Poly(1,2-Diketones), all with a Molecular Weight Greater than 100 (O-O Bidentates, O-O Tridentates, O-O Tetridentates)	R-C(=O)-C(=O)-R' where R and R' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms. If these ligands exhibit a molecular weight less than or equal to 100, the solubility of the resultant diketone complex will be too high.
<u>O Valence Stabilizer #8:</u> Malonamides (Malonodiamides), Bis(malonamides), and Polymalonamides (O-O Bidentates, O-O Tridentates, O-O Tetridentates)	RR'-N-C(=O)-CR''R''''-C(=O)-N-R'''''R'''''' where R, R', R'', R'''', R'''''', and R''''''' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>O Valence Stabilizer #9:</u> 2-Acylacetamides, Bis(2-acylacetamides), and Poly(2-acylacetamides) (O-O Bidentates, O-O Tridentates, O-O	RR'-N-C(=O)-CR''R''''-C(=O)-R''''' where R, R', R'', R'''', and R'''' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally

Tetradentates)	having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>O Valence Stabilizer #10:</u> Monothiodicarbonic Diamides, Bis(monothiodicarbonic diamides), and Poly(monothiodicarbonic diamides) (O-O Bidentates, O-O Tridentates, O-O Tetradentates)	RR'-N-C(=O)-S-C(=O)-N-R''R''' where R, R', R'', and R''' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>O Valence Stabilizer #11:</u> Monothiodicarbonic Acids, Bis(monothiodicarbonic acids), Poly(monothiodicarbonic acids), and derivatives thereof (O-O Bidentates, O-O Tridentates, O-O Tetradentates)	R-O-C(=O)-S-C(=O)-O-R', where R and R' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>O Valence Stabilizer #12:</u> Trithionic acid, Bis(trithionic acid), Poly(trithionic acid), and derivatives thereof (O-O Bidentates, O-O Tridentates, O-O Tetradentates)	R-O-S(=O)(=O)-S-S(=O)(=O)-O-R', where R and R' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>O Valence Stabilizer #13:</u> Hypophosphoric Acids, Bis(hypophosphoric acids), and Poly(hypophosphoric acids), and derivatives thereof (O-O Bidentates, O-O Tridentates, O-O Tetradentates)	(R-O-)(R'-O-)P(=O)-P(=O)(-O-R'')(-O-R'''), where R, R', R'', and R''' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms. Note: these ligands are not to be confused with hypophosphorous acid derivatives (hypophosphites) (R-O-)R''R'''P(=O) which are very reducing and therefore unacceptable for stabilization of high valence states in metal ions.
<u>O Valence Stabilizer #14:</u> Hypophosphoramides, Bis(hypophosphoramides), and Poly(hypophosphoramides) (O-O Bidentates, O-O Tridentates, O-O	(RR'-N-)(R''R''"-N-)P(=O)-P(=O)(-N-R''''R''''')(N-R''''''R'''''''), where R, R', R'', R''', R''''', R''''''', and R'''''''' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40,

Tetridentates)	optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms. Note: these ligands are not to be confused with hypophosphorous acid derivatives (hypophosphites) ($R-O-R''P(=O)$) which are very reducing and therefore unacceptable for stabilization of high valence states in metal ions.
<u>O Valence Stabilizer #15:</u> Imidodiphosphoric Acids, Hydrazidodiphosphoric Acids, Bis(imidodiphosphoric Acids), Bis(hydrazidodiphosphoric Acids), Poly(imidodiphosphoric Acids), Poly(hydrazidodiphosphoric Acids), and derivatives thereof (O-O Bidentates, O-O Tridentates, O-O Tetridentates)	($R-O-(R'-O)P(=O)-NH-P(=O)(-O-R'')$) ($-O-R'''$) for imidodiphosphoric acids, and ($R-O-(R'-O)P(=O)-NH-NH-P(=O)(-O-R'')$) ($-O-R'''$) for hydrazidodiphosphoric acids; where R, R', R'', and R''' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>O Valence Stabilizer #16:</u> Imidodiphosphoramides, Hydrazidodiphosphoramides, Bis(imidodiphosphoramides), Bis(hydrazidodiphosphoramides), Poly(imidodiphosphoramides), and Poly(hydrazidodiphosphoramides) (O-O Bidentates, O-O Tridentates, O-O Tetridentates)	($RR'-N-(R''R'''-N-)P(=O)-NH-P(=O)(-N-R''''R''''')$) ($-N-R''''''R''''''$) for imidodiphosphoramides, and $-NH-NH-$ derivatives for hydrazidodiphosphoramides, where R, R', R'', R''', R''''', R''''''', R''''''''', and R''''''''' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>O Valence Stabilizer #17:</u> Diphosphoramides, Bis(diphosphoramides), and Poly(diphosphoramides) (O-O Bidentates, O-O Tridentates, O-O Tetridentates)	($RR'-N-(R''R'''-N-)P(=O)-O-P(=O)(-N-R''''R''''')$) ($-N-R''''''R''''''$), where R, R', R'', R''', R''''', R''''''', and R''''''''' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>O Valence Stabilizer #18:</u> Beta-Hydroxyketones, Beta-Hydroxyaldehydes, Bis(beta-hydroxyketones), Bis(beta-hydroxyaldehydes), Poly(beta-	$R-CR'(-OH)-CH_2-C(=O)-R''$, where R, R', and R'' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-

hydroxyketones), and Poly(beta-hydroxyaldehydes) (O-O Bidentates, O-O Tridentates, O-O Tetridentates)	insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>O Valence Stabilizer #19:</u> Oxamides, Bis(oxamides), and Poly(oxamides) (O-O Bidentates, O-O Tridentates, O-O Tetridentates)	$\text{RR}'-\text{N}-\text{C}(=\text{O})-\text{C}(=\text{O})-\text{N}-\text{R}''\text{R}'''$, where R, R', R'', and R''' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>O Valence Stabilizer #20:</u> Squaric Acids and derivatives thereof (O-O Bidentates)	$-\text{C}(-\text{OH})=\text{C}(-\text{OH})-$, where the two carbon atoms supporting the hydroxy groups are included within a cyclic hydrocarbon moiety, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>O Valence Stabilizer #21:</u> Dicarboxylic Acids, Bis(dicarboxylic acids), Poly(dicarboxylic acids), and derivatives thereof (O-O Bidentates and O-O Tetridentates)	$(\text{R}-\text{O}-)(\text{O}=\text{)}\text{C}-\text{R}'-\text{C}(=\text{O})(-\text{O}-\text{R}')$, where R, R', and R'' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>O Valence Stabilizer #22:</u> Carbonates and Bis(carbonates) (O-O Bidentates and O-O Tetridentates)	$\text{R}-\text{O}-\text{C}(=\text{O})-\text{O}-\text{R}'$, where R, and R' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>O Valence Stabilizer #23:</u> Carbamates, Bis(carbamates), and Poly(carbamates) (including N-hydroxycarbamates and N-mercaptocarbamates) (O-O Bidentates, O-O Tridentates, and O-O Tetridentates)	$\text{RR}'\text{N}^+=\text{C}(\text{OH})(\text{OH})$, where R and R' represent H, OH, SH, OR'' (R'' = C ₁ -C ₃₀ alkyl or aryl), SR'' (R'' = C ₁ -C ₃₀ alkyl or aryl), NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>O Valence Stabilizer #24:</u> Carbimates, Bis(carbimates), and Poly(carbimates) (O-O Bidentates, O-O Tridentates, and O-O Tetridentates)	$\text{RN}=\text{C}(\text{OH})(\text{OH})$, where R represents H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or

	water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
O Valence Stabilizer #25: N-(Aminomethylol)ureas [N-(Aminohydroxymethyl)ureas], Bis[N-(aminomethylol)ureas], and Poly[N-(aminomethylol)ureas] (O-O Bidentates, O-O Tridentates, O-O Tetridentates)	RR'-N-CH(-OH)-NR"-C(=O)-NR'''R''", where R, R', R", R"', and R''' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
O Valence Stabilizer #26: Cyanate ligands (O Monodentates)	Cyanates bound directly to the high valence metal ion.
N-S Valence Stabilizer #1: Diformamidine Disulfides (Thioperoxydicarbonimidic Diamides or Dihydrazides), Thioperoxytricarbonimidic Diamides or Dihydrazides, Thioperoxytetracarbonimidic Diamides or Dihydrazides, Bis(diformamidine disulfides), and Poly(diformamidine disulfides) (N-S Bidentates, N-S Tridentates, N-S Tetridentates)	RR'-N-C(=NH)-S-S-C(=NH)-NR'''R''", where R, R', R", and R''' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
N-S Valence Stabilizer #2: S-Amidinodithiocarbamates, Bis(S-amidinodithiocarbamates), and Poly(S-amidinodithiocarbamates) (N-S Bidentates and N-S Tetridentates)	RR'-N-C(=NH)-S-CS-NR'''R''", where R, R', R", and R''' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
N-S Valence Stabilizer #3: O-Amidinothiocarbamates, Bis(O-amidinothiocarbamates), and Poly(O-amidinothiocarbamates) (N-S Bidentates and N-S Tetridentates)	RR'-N-C(=NH)-O-CS-NR'''R''", where R, R', R", and R''' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
N-S Valence Stabilizer #4: S-Amidinoperoxythiocarbamates, Bis(S-amidinoperoxythiocarbamates), and Poly(S-amidinoperoxythiocarbamates) (N-S Bidentates and N-S Tetridentates)	RR'-N-C(=NH)-S-S-CS-NR'''R''", where R, R', R", and R''' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.

	P atoms.
<u>N-S Valence Stabilizer #5:</u> Phosphorimidothioic Acid; Phosphorimidodithioic Acid; Phosphorimidotriethioic Acid; Bis(Phosphorimidothioic Acid); Bis(Phosphorimidodithioic Acid); Bis(Phosphorimidotriethioic Acid); Poly(Phosphorimidothioic Acid); Poly(Phosphorimidodithioic Acid); Poly(Phosphorimidotriethioic Acid); and derivatives thereof (N-S Bidentates and N-S Tetridentates)	(NH=)P(-SR)(-OR')(-OR") for phosphorimidothioic acid, (NH=)P(-SR)(-SR')(-OR") for phosphorimidodithioic acid, (NH=)P(-SR)(-SR')(-SR") for phosphorimidotriethioic acid, where R, R', and R" represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-S Valence Stabilizer #6:</u> Phosphorothioic Triamides, Bis(phosphorothioic triamides), and Poly(phosphorothioic triamides) (N-S Bidentates and N-S Tetridentates)	(S=)P(-NRR')(-NR"R'')(-NR'''R'''), where R, R', R'', R''', and R'''' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-S Valence Stabilizer #7:</u> Phosphoramidotriethioic Acid, Phosphorodiamidodithioic Acid, Bis(phosphoramidotriethioic acid), Bis(phosphorodiamidodithioic acid), poly(phosphoramidotriethioic acid), poly(phosphorodiamidodithioic acid), and derivatives thereof (N-S Bidentates and N-S Tetridentates)	(S=)P(-NRR')(-SR")(-SR'''') for phosphoramidotriethioic acid, and (S=)P(-NRR')(-NR"R'')(-SR''') for phosphorodiamidodithioic acid, where R, R', R'', R''', and R'''' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-S Valence Stabilizer #8:</u> Phosphoramidothioic Acid, Phosphoramidodithioic Acid, Phosphorodiamidothioic Acid, Bis(Phosphoramidothioic Acid), Bis(Phosphoramidodithioic Acid), Bis(Phosphorodiamidothioic Acid), Poly(Phosphoramidothioic Acid), Poly(Phosphoramidodithioic Acid), and Poly(Phosphorodiamidothioic Acid) (N-S Bidentates and N-S Tetridentates)	(O=)P(-NRR')(-SR")(-OR''') or (S=)P(-NRR')(-OR")(-OR''') for phosphoramidothioic acid; (O=)P(-NRR')(-SR")(-SR''') or (S=)P(-NRR')(-SR")(-OR''') for phosphoramidodithioic acid; (O=)P(-NRR')(-NR"R'')(-SR''') or (S=)P(-NRR')(-NR"R'')(-OR''') for phosphorodiamidothioic acid, where R, R', R'', R''', and R'''' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.

<u>N-S Valence Stabilizer #9:</u> N-Thioacyl 7-Aminobenzylidenimines (N-S Bidentates or N-S Tetradentates)	R'-C(=S)-N=C(-R)(-NHR''), where R is an aromatic derivative (i.e., -C ₆ H ₅), and R' and R'' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-S Valence Stabilizer #10:</u> Thiohydroxamates (Thiohydroxylamines), Bis(thiohydroxamates), and Poly(thiohydroxamates) (N-S Bidentates, N-S Tetradentates, and N-S Hexadentates)	R-C(=S)-NR'-OH or R-C(-SH)=N-OH, where R and R' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-S Valence Stabilizer #11:</u> Alpha- or ortho-Aminothiocarboxylic Acids, and alpha- or ortho-Aminothiodicarboxylic Acids, and derivatives thereof (N-S Bidentates, N-S Tridentates, and N-S Tetradentates)	R-CH(-NHR')-C(=S)(-OH) or R-CH(-NHR')-C(=S)(-SH) for aminothiocarboxylic acids, and (HO-)(S=)C-CH(-NHR)-R'-CH(-NHR'')-C(=S)(-OH) or (HS-)(S=)C-CH(-NHR)-R'-CH(-NHR'')-C(=S)(-SH) for aminothiodicarboxylic acids, where R, R', and R'' represent any organic functional group wherein the number of carbon atoms ranges from 1 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-S Valence Stabilizer #12:</u> Thiosemicarbazones, Bis(thiosemicarbazones), and Poly(thiosemicarbazones) (N-S Bidentates, N-S Tetradentates, and N-S Hexadentates)	RR'-N-C(=S)-NR''-N=CR'''R''', where R, R', R'', R''', and R''' represent H, or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-S Valence Stabilizer #13:</u> Thioacyl hydrazones, Bis(thioacyl hydrazones), and Poly(thioacyl hydrazones) (N-S Bidentates, N-S Tetradentates, and N-S Hexadentates)	R-C(=S)-NR'-N=CR'''R''', where R, R', R'', and R''' represent H, or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-S Valence Stabilizer #14:</u>	R-N=N-C(=S)-NR'-NR''R'', where R, R', R'',

<p>Thiocarbazones (Diazene carbothioic hydrazides), Bis(thiocarbazones), and Poly(thiocarbazones) (N-S Bidentates, N-S Tetridentates, and N-S Hexadentates)</p>	<p>and R[”] represent H, or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.</p>
<p>N-S Valence Stabilizer #15: Azo compounds including triazenes with thiol or mercapto or thiocarbonyl substitution at the ortho- (for aryl) or alpha- or beta- (for alkyl) positions, Bis[o-(HS-)] or alpha- or beta-(HS-)azo compounds], or Poly[o-(HS-)] or alpha- or beta-(HS-)azo compounds) (N-S Bidentates, N-S Tridentates, N-S Tetridentates, or N-S Hexadentates)</p>	<p>R-N=N-R' for azo compounds, R-N=N-NH-R' for triazenes, where R, and R' represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. (Must include ortho-thio, mercapto, or thiocarbonyl substituted aryl azo compounds, and alpha- or beta-thio, mercapto, or thiocarbonyl alkyl azo compounds.) Ligand can also contain nonbinding N, O, S, or P atoms.</p>
<p>N-S Valence Stabilizer #16: Diazeneformothioamides, Diazeneacetothioamides, Bis(diazeneformothioamides), Bis(diazeneacetothioamides), Poly(diazeneformothioamides), and Poly(diazeneacetothioamides) (N-S Bidentates, N-S Tetridentates, and N-S Hexadentates)</p>	<p>R-N=N-C(=S)-NR'R'' for diazeneformothioamides, and R-N=N-CR'R''-C(=S)-NR'''R''' for diazeneacetothioamides, where R, R', R'', R''', and R''' represent H, NH₂, or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.</p>
<p>N-S Valence Stabilizer #17: Diazene carbothioic acids, Diazene carbodithioic acids, Bis(diazene carbothioic acids), Bis(diazene carbodithioic acids), Poly(diazene carbothioic acids), Poly(diazene carbodithioic acids) and derivatives thereof (N-S Bidentates, N-S Tetridentates, N-S Hexadentates)</p>	<p>R-N=N-C(=S)-O-R' or R-N=N-CR'R''-C(=S)-O-R''' for diazene carbothioic acids, and R-N=N-C(=S)-S-R' or R-N=N-CR'R''-C(=S)-S-R''' for diazene carbodithioic acids, where R, R', R'', and R''' represent H, NH₂, or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.</p>
<p>N-S Valence Stabilizer #18: Diazeneformothioaldehydes, Diazeneacetothioaldehydes, Bis(diazeneformothioaldehydes), Bis(diazeneacetothioaldehydes), Poly(diazeneformothioaldehydes), and Poly(diazeneacetothioaldehydes) (N-S</p>	<p>R-N=N-C(=S)-R' for diazeneformothioaldehydes, and R-N=N-CR'R''-C(=S)-R''' for diazeneacetothioaldehydes, where R, R', R'', and R''' represent H, NH₂, or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having</p>

Bidentates, N-S Tetridentates and N-S Hexadentates)	halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-S Valence Stabilizer #19:</u> Diazenediformothioamides, Diazenediacetothioamides, Bis(diazenediformothioamides), Bis(diazenediacetothioamides), Poly(diazenediformothioamides), and Poly(diazenediacetothioamides) (N-S Tridentates and N-S Hexadentates)	RR'-N-C(=S)-N=N-C(=S)-NR''R''' or RR'-N-C(=S)-N=N-C(=O)-NR''R''' for diazenediformothioamides, and RR'-N-C(=S)-CR''R''-N=N-CR''''R''''-C(=S)-NR'''''R'''''' or RR'-N-C(=S)-CR''R''-N=N-CR''''R''''-C(=O)-NR'''''R'''''' for diazenediacetothioamides, where R, R', R'', R''', R''''', R'''''', and R''''''' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-S Valence Stabilizer #20:</u> Diazenedicarbothioic acids, Diazenedicarbodithioic acids, Bis(diazenedicarbothioic acids), Bis(diazenedicarbodithioic acids), Poly(diazenedicarbothioic acids), Poly(diazenedicarbodithioic acids) and derivatives thereof (N-S Tridentates and N-S Hexadentates)	R-O-C(=S)-N=N-C(=S)-O-R', R-O-C(=S)-CR'R''-N=N-CR''''R''''-C(=S)-O-R'''''', R-O-C(=S)-N=N-C(=O)-O-R', or R-O-C(=S)-CR'R''-N=N-CR''''R''''-C(=O)-O-R''''' for diazenedicarbothioic acids, and R-S-C(=S)-N=N-C(=S)-S-R' or R-S-C(=S)-CR'R''-N=N-CR''''R''''-C(=S)-S-R''''' for diazenedicarbodithioic acids, where R, R', R'', R''', R''''', and R''''''' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-S Valence Stabilizer #21:</u> Diazenediformothioaldehydes, Diazenediacetothioaldehydes, Bis(diazenediformothioaldehydes), Bis(diazenediacetothioaldehydes), Poly(diazenediformothioaldehydes), and Poly(diazenediacetothioaldehydes) (N-S Tridentates and N-S Hexadentates)	RC(=S)-N=N-C(=S)-R' or RC(=S)-N=N-C(=O)-R' for diazenediformothioaldehydes, and RC(=S)-CR'R''-N=N-CR''''R''''-C(=S)-R''''' or RC(=S)-CR'R''-N=N-CR''''R''''-C(=O)-R''''' for diazenediacetothioaldehydes, where R, R', R'', R''', and R'''' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-S Valence Stabilizer #22:</u>	R-N=N-CR'=N-NR''R''', where R, R', R'', and

<p>Ortho-thio (or -mercapto) Substituted Formazans, Bis(o-thio or -mercapto substituted formazans), and Poly(o-thio or -mercapto substituted formazans) (N-S Bidentates, N-S Tridentates, N-S Tetridentates, and N-S Hexadentates)</p>	<p>R^{'''} represent H, or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. (Must include ortho-thio or mercapto substituted aryl R derivatives, and beta-thio or mercapto substituted alkyl R derivatives.) Ligand can also contain nonbinding N, O, S, or P atoms.</p>
<p><u>N-S Valence Stabilizer #23:</u> Ortho-thio (or -mercapto) Substituted Azines (including ketazines), Bis(o-thio or mercapto substituted azines), and Poly(o-thio or mercapto substituted azines) (N-S Bidentates, N-S Tridentates, N-S Tetridentates, and N-S Hexadentates)</p>	<p>RR'C=N-N=CR''R^{'''} or RR'C=N-NR''R^{'''} (for ketazines), where R, R', R'', and R^{'''} represent H, or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. (Must include ortho-thio or mercapto substituted aryl R derivatives, and beta-thio or mercapto substituted alkyl R derivatives.) Ligand can also contain nonbinding N, O, S, or P atoms.</p>
<p><u>N-S Valence Stabilizer #24:</u> Schiff Bases with one Imine (C=N) Group and with ortho- or alpha- or beta-thio or mercapto or thiocarbonyl substitution (N-S Bidentates, N-S Tridentates, N-S Tetridentates, N-S Pentadentates, or N-S Hexadentates). Also includes Schiff Bases derived from the reaction of carbonyl compounds with dithiocarbazates, and hydrazones with ortho-S substitution.</p>	<p>RR'C=N-R'', where R, R', and R'' represent H, or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. (Must contain ortho- or alpha- or beta-thio or mercapto or thiocarbonyl substitution.) Ligand can also contain nonbinding N, O, S, or P atoms.</p>
<p><u>N-S Valence Stabilizer #25:</u> Schiff Bases with two Imine (C=N) Groups and with ortho- or alpha- or beta-thio or mercapto or thiocarbonyl substitution (N-S Tridentates, N-S Tetridentates, N-S Pentadentates, or N-S Hexadentates). Also includes Schiff Bases derived from the reaction of carbonyl compounds with dithiocarbazates, and hydrazones with ortho-S substitution.</p>	<p>RR'C=N-R''-N=CR''''R^{'''} or R-N=C-R'-C=N-R' or RC=N-R'-N=CR'', where R, R', R'', R''', and R^{'''} represent H, or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. (Must contain ortho- or alpha- or beta-thio or mercapto or thiocarbonyl substitution.) Ligand can also contain nonbinding N, O, S, or P atoms.</p>
<p><u>N-S Valence Stabilizer #26:</u> Schiff Bases with three Imine (C=N) Groups and with ortho- or alpha- or beta-thio or mercapto or thiocarbonyl</p>	<p>N(-R-N=CR'R'')₃, where R, R', and R'' represent H, or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or</p>

<p>substitution (N-S Tetridentates, N-S Pentadentates, or N-S Hexadentates). Also includes Schiff Bases derived from the reaction of carbonyl compounds with dithiocarbazates, and hydrazones with ortho-S substitution.</p>	<p>polarizing or water-insolubilizing/solubilizing groups attached. (Must contain ortho- or alpha- or beta-thio or mercapto or thiocarbonyl substitution.) Ligand can also contain nonbinding N, O, S, or P atoms.</p>
<p><u>N-S Valence Stabilizer #27:</u> Thioalkyl Amines (Aminothiols or Aminodisulfides) and Thioalkyl Imines (Iminothiols or Iminodisulfides) (N-S Bidentates, N-S Tridentates, N-S Tetridentates, and N-S Hexadentates)</p>	<p>[R-CR'(-NR''R'')]x-R'''-[C(-SR''')R''''R''''']y, [R-CR'(-NR''R'')]x-R'''-[C(-S-S-R''')R''''R''''']y, or [R-CR'(-NR''R'')]x-R'''-[C(=S)R''''']y for thioalkyl amines; and [R-C(=NR')]x-R'''-[C(-SR'')R''''R''''']y, [R-C(=NR')]x-R'''-[C(-SR'')R''''R''''']y, or [R-C(=NR')]x-R'''-[C(=S)R''''']y for thioalkyl imines, where R, R', R'', R''', R''''', R''''''', and R''''''' represent H, NH₂, or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached, and x and y = 1-6. Ligand can also contain inenonbinding N, O, S, or P atoms.</p>
<p><u>N-S Valence Stabilizer #28:</u> Thioaryl Amines and Thioaryl Imines (N-S Bidentates, N-S Tridentates, N-S Tetridentates, and N-S Hexadentates)</p>	<p>[R(-NR'R')(-SR'')], [R(-NR'R')(-S-S-R'')], [R(-NR'R')(-C(=S)R'')], [R(-NR'R')_x]₂S, [R(-NR'R')_x]₂₋₃R''(-SR''')y, [R(-SR')_x]₂₋₃R''(-NR''R''')y, [R(-NR'R')_x]₂S₂, and [R(-NR'R')_x]₂R''(C(=S))_yR''' for thioaryl amines; and [R(-SR')_x]₂NH or [R(-SR')_x]₂NHNH for thioaryl imines, where R, R', R'', R''', and R'''' represent H, NH₂, or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached, and x = 0-2 and y = 1-4. Ligand can also contain nonbinding N, O, S, or P atoms.</p>
<p><u>N-S Valence Stabilizer #29:</u> Five-Membered Heterocyclic Rings containing One, Two, Three, or Four Nitrogen Atoms at least one additional Sulfur Atom Binding Site not in a Ring (N-S Bidentates, N-S Tridentates, N-S Tetridentates, or N-S Hexadentates)</p>	<p>Five membered heterocyclic ring(s) containing one, two, three, or four nitrogen atoms. In addition, ligand contains additional sulfur-containing substituents (usually thiols, mercaptans, disulfides, or thiocarbonyls) that constitute S binding sites. Can include other ring systems bound to the heterocyclic ring or to the S-containing substituent, but they do not coordinate with the stabilized, high valence metal ion. Ring(s) can also contain O, S, or P atoms. This 5-membered ring(s) and/or</p>

	attached, uncoordinating rings and/or S-containing substituent(s) may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>N-S Valence Stabilizer #30:</u> Six-Membered Heterocyclic Rings containing One, Two, Three, or Four Nitrogen Atoms at least one additional Sulfur Atom Binding Site not in a Ring (N-S Bidentates, N-S Tridentates, N-S Tetridentates, or N-S Hexadentates)	Six membered heterocyclic ring(s) containing one, two, three, or four nitrogen atoms. In addition, ligand contains additional sulfur-containing substituents (usually thiols, mercaptans, disulfides, or thiocarbonyls) that constitute S binding sites. Can include other ring systems bound to the heterocyclic ring or to the S-containing substituent, but they do not coordinate with the stabilized, high valence metal ion. Ring(s) can also contain O, S, or P atoms. This 6-membered ring(s) and/or attached, uncoordinating rings and/or S-containing substituent(s) may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>N-S Valence Stabilizer #31:</u> Five-Membered Heterocyclic Rings containing One or Two Sulfur Atoms at least one additional Nitrogen Atom Binding Site not in a Ring (N-S Bidentates, N-S Tridentates, N-S Tetridentates, or N-S Hexadentates)	Five membered heterocyclic ring(s) containing one or two sulfur atoms. In addition, ligand contains additional nitrogen-containing substituents (usually amines, imines, or hydrazides) that constitute N binding sites. Can include other ring systems bound to the heterocyclic ring or to the N-containing substituent, but they do not coordinate with the stabilized, high valence metal ion. Ring(s) can also contain O, S, or P atoms. This 5-membered ring(s) and/or attached, uncoordinating rings and/or N-containing substituent(s) may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>N-S Valence Stabilizer #32:</u> Six-Membered Heterocyclic Rings containing One or Two Sulfur Atoms at least one additional Nitrogen Atom Binding Site not in a Ring (N-S Bidentates, N-S Tridentates, N-S Tetridentates, or N-S Hexadentates)	Six membered heterocyclic ring(s) containing one or two sulfur atoms. In addition, ligand contains additional nitrogen-containing substituents (usually amines, imines, or hydrazides) that constitute N binding sites. Can include other ring systems bound to the heterocyclic ring or to the N-containing substituent, but they do not coordinate with the stabilized, high valence metal ion. Ring(s) can also contain O, S, or P atoms. This 6-membered ring(s) and/or attached, uncoordinating rings and/or N-containing substituent(s) may or may not have halogen or polarizing or water-

<u>N-S Valence Stabilizer #33:</u> Five-Membered Heterocyclic Rings containing One, Two, Three, or Four Nitrogen Atoms at least one additional Sulfur Atom Binding Site in a Separate Ring (N-S Bidentates, N-S Tridentates, N-S Tetridentates)	insolubilizing/solubilizing groups attached. Five membered heterocyclic ring(s) containing one, two, three, or four nitrogen atoms. In addition, ligand contains additional sulfur-containing rings that constitute S binding sites. Can include other ring systems bound to the N- or S-containing heterocyclic rings, but they do not coordinate with the stabilized, high valence metal ion. Ring(s) can also contain O, S, or P atoms. This 5-membered ring(s) and/or additional S-containing ring(s) and/or attached, uncoordinating rings may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>N-S Valence Stabilizer #34:</u> Six-Membered Heterocyclic Rings containing One, Two, Three, or Four Nitrogen Atoms at least one additional Sulfur Atom Binding Site in a Separate Ring (N-S Bidentates, N-S Tridentates, N-S Tetridentates)	Six membered heterocyclic ring(s) containing one, two, three, or four nitrogen atoms. In addition, ligand contains additional sulfur-containing rings that constitute S binding sites. Can include other ring systems bound to the N- or S-containing heterocyclic rings, but they do not coordinate with the stabilized, high valence metal ion. Ring(s) can also contain O, S, or P atoms. This 6-membered ring(s) and/or additional S-containing ring(s) and/or attached, uncoordinating rings may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>N-S Valence Stabilizer #35:</u> Two-, Three-, Four-, Six-, Eight-, and Ten-Membered Macrocyclics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Nitrogen (usually amine or imine groups) or Sulfur (usually thiols, mercaptans, or thiocarbonyls) and are not contained in Component Heterocyclic Rings (N-S Bidentates, N-S Tridentates, N-S Tetridentates, and N-S Hexadentates)	Macrocyclic ligands containing two, three, four, six, eight, or ten binding sites composed of nitrogen and sulfur to valence stabilize the central metal ion. Can include other hydrocarbon or ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbons/rings may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>N-S Valence Stabilizer #36:</u> Four-, Six-, Eight-, or Ten-Membered Macrocyclics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Nitrogen or Sulfur and are contained in	Macrocyclic ligands containing a total of four, six, eight, or ten heterocyclic rings containing nitrogen or sulfur binding sites. Can include other hydrocarbon/ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating

Component Heterocyclic Rings (N-S Bidentates, N-S Tridentates, N-S Tetridentates, or N-S Hexadentates)	hydrocarbon/rings may or may not have halogen or polarizing or water-insolubilizing groups attached.
<u>N-S Valence Stabilizer #37:</u> Four-, Six-, Eight-, or Ten-Membered Macrocyclics, Macroyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Nitrogen or Sulfur and are contained in a Combination of Heterocyclic Rings and Amine, Imine, Thiol, Mercapto, or Thiocarbonyl Groups (N-S Bidentates, N-S Tridentates, N-S Tetridentates, or N-S Hexadentates)	Macrocyclic ligands containing at least one heterocyclic ring. These heterocyclic rings provide nitrogen or sulfur binding sites to valence stabilize the central metal ion. Other amine, imine, thiol, mercapto, or thiocarbonyl binding sites can also be included in the macrocyclic ligand, so long as the total number of binding sites is four, six, eight, or ten. Can include other hydrocarbon/ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbon/rings may or may not have halogen or polarizing or water-insolubilizing groups attached.
<u>N-O Valence Stabilizer #1:</u> N-Hydroxy(or N,N'-dihydroxy)amidines and N-Hydroxy(or N,N'-dihydroxy)diamidines (N-O Bidentates, N-O Tridentates, or N-O Tetridentates)	R'-N(-OH)-C(-R)=N-R'', where R, R', and R'' represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #2:</u> Guanylureas, Guanidinoureas, Bis(guanylureas), Bis(guanidinoureas), Poly(guanylureas), and Poly(guanidinoureas) (N-O Bidentates and N-O Tetridentates)	RR'-N-C(=NH)-NR''-CO-NR'''R'''' for guanylureas, and RR'-N-C(=NH)-NR''-NH-CO-NR'''R'''' for guanidinoureas, where R, R', R'', R''', and R'''' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #3:</u> Amidinoamides, Guanidinoamides, Bis(amidinoamides), Bis(guanidinoamides), Poly(amidinoamides), and Poly(guanidinoamides) (including both N-amidinoamides and 2-amidinoacetamides) (N-O Bidentates and N-O Tetridentates)	RR'-N-C(=NH)-NR''-CO-R'' for N-amidinoamides, or RR'-N-C(=NH)-CR''R''-CO-N-R''''R''''' for 2-amidinoacetamides, and RR'-N-C(=NH)-NR''-NH-CO-R'' for guanidinoamides, where R, R', R'', R''', R'''', and R''''' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.

	P atoms.
<u>N-O Valence Stabilizer #4:</u> Imidoylamides, Bis(imidoylamides), and Poly(imidoylamides) (N-O Bidentates and N-O Tetridentates)	R-C(=NH)-NR'-CO-R'', where R, R', and R'', represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #5:</u> O-Amidinocarbamates, Bis(O-amidinocarbamates), and Poly(O-amidinocarbamates) (N-O Bidentates and N-O Tetridentates)	RR'-N-C(=NH)-O-CO-NR''R''', where R, R', R'', and R''' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #6:</u> S-Amidinothiocarbamates, Bis(S-amidinothiocarbamates), and Poly(S-amidinothiocarbamates) (N-O Bidentates and N-O Tetridentates)	RR'-N-C(=NH)-S-CO-NR''R''', where R, R', R'', and R''' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #7:</u> Diimidosulfuric Acid, Bis(diimidosulfuric acid), and derivatives thereof (N-O Bidentates and N-O Tetridentates)	(NH=)(NH=)P(OR)(OR'), where R, R', and R'' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #8:</u> Phosphorimidic Acid, Bis(phosphorimidic acid); and Poly(phosphorimidic acid), and derivatives thereof (N-O Bidentates)	(NH=)P(-OR)(-OR')(-OR''), where R, R', and R'' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #9:</u> Phosphoric Triamides, Bis(phosphoric triamides), and Poly(phosphoric triamides) (N-O Bidentates and N-O Tetridentates)	(O=)P(-NRR')(-NR''R''')(-NR''''R'''''), where R, R', R'', R''', and R''''' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups

	attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #10:</u> Phosphoramidic Acid, Phosphorodiamidic Acid, Bis(phosphoramidic acid), Bis(phosphorodiamidic acid), Poly(phosphoramidic acid), Poly(phosphorodiamidic acid), and derivatives thereof (N-O Bidentates and N-O Tetridentates)	(O=)P(-NRR')(-OR")(-OR'") for phosphoramidic acid and (O=)P(-NRR')(-NR"R'")(-OR'") for phosphorodiamidic acid, where R, R', R", R"', and R''' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #11:</u> N-Acyl 7-Aminobenzylidenimines (N-O Bidentates or N-O Tetridentates)	R'-C(=O)-N=C(-R)(-NHR"), where R is an aromatic derivative (i.e., -C ₆ H ₅), and R' and R" represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #12:</u> Oximes, Dioximes, and Poly(oximes) (N-O Bidentates, N-O Tridentates, and N-O Tetridentates)	R-C(=NOH)-R' for oximes, and R-C(=NOH)-C(=NOH)-R' for dioximes, where R and R' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #13:</u> Carbonyl oximes, Bis(carbonyl oximes), and Poly(carbonyl oximes) (N-O Bidentates, N-O Tridentates, and N-O Tetridentates)	R-C(=O)-C(=NOH)-R', where R and R' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #14:</u> Imine oximes, Bis(imine oximes), and Poly(imine oximes) (including 2-nitrogen heterocyclic oximes) (N-O Bidentates, N-O Tridentates, N-O Tetridentates, and N-O Hexadentates)	R-C(=N-R")-C(=NOH)-R', where R, R', and R" represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.

<u>N-O Valence Stabilizer #15:</u> Hydroxy oximes, Bis(hydroxy oximes), and Poly(hydroxy oximes) (including 2-oxygen heterocyclic oximes) (N-O Bidentates, N-O Tridentates, N-O Tetridentates, and N-O Hexadentates)	R-CH(-OH)-C(=NOH)-R', where R, R', and R'' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #16:</u> Amino oximes, Bis(amino oximes), and Poly(amino oximes) (N-O Bidentates, N-O Tridentates, N-O Tetridentates, and N-O Hexadentates)	RR'-C(-NH-R")-C(=NOH)-R'''', where R, R', R'', and R''' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #17:</u> Amido oximes, Bis(amido oximes), and Poly(amido oximes) (N-O Bidentates, N-O Tridentates, N-O Tetridentates, and N-O Hexadentates)	RR'-N-C(=NOH)-R'', where R, R', and R'' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #18:</u> Azo oximes, Bis(azo oximes), and Poly(azo oximes) (N-O Bidentates, N-O Tridentates, N-O Tetridentates, and N-O Hexadentates). Also includes hydrazone oximes.	R-N=N-C(=NOH)-R' or RR'C=N-NR"-C(=NOH)-R''', where R, R', R'', and R''' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. (R is typically an aryl group.) Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #19:</u> 2-Nitrosophenols (o-Quinone monoximes) (N-O Bidentates)	o-(ON-)(HO-)Ar, where Ar represents an aromatic group or heterocyclic wherein the number of carbon atoms ranges from 6 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #20:</u> 2-Nitrophenols (N-O Bidentates)	o-(O ₂ N-)(HO-)Ar, where Ar represents an aromatic group or heterocyclic wherein the number of carbon atoms ranges from 6 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N,

	O, S, or P atoms.
<u>N-O Valence Stabilizer #21:</u> Hydroxamates (Hydroxylamines), Bis(hydroxamates), and Poly(hydroxamates) (N-O Bidentates, N-O Tetridentates, and N-O Hexadentates)	R-C(=O)-NR'-OH or R-C(-OH)=N-OH, where R and R' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #22:</u> N-Nitrosohydroxylamines, Bis(N-nitrosohydroxylamines), and Poly(N-nitrosohydroxylamines) (N-O Bidentates, N-O Tetridentates, and N-O Hexadentates)	R-N(-NO)-OH, where R represents any organic functional group wherein the number of carbon atoms ranges from 1 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. (R is typically an aryl or heterocyclic group.) Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #23:</u> Amino Acids and ortho-Aminocarboxylic Acids, Peptides, Polypeptides, and Proteins [N-O Bidentates, N-O Tridentates, and N-O Tetridentates; possibly S-O dentates for sulfur-contg. examples such as penicillamine and cystine]	R-CH(-NHR')-C(=O)(-OH) for amino acids and ortho-aminocarboxylic acids, and R-CH(-NHR')-C(=O)-(NR")-CH(-R")-C(=O)(-OH) for peptides, where R, R', R", and R"" represent any organic functional group wherein the number of carbon atoms ranges from 1 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #24:</u> Amides, Bis(amides), and Poly(amides), including lactams (N-O Bidentates, N-O Tridentates, and N-O Tetridentates)	RCONR'R", where R, R', and R" represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #25:</u> Semicarbazones, Bis(semicarbazones), and Poly(semicarbazones) (N-O Bidentates, N-O Tetridentates, and N-O Hexadentates)	RR'-N-C(=O)-NR"-N=CR""R""", where R, R', R", R", and R"" represent H, or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #26:</u> Acyl hydrazones, Bis(acyl hydrazones), and Poly(acyl hydrazones) (N-O Bidentates, N-O Tetridentates, and N-O Hexadentates)	R-C(=O)-NR'-N=CR"R""", where R, R', R", and R"" represent H, or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen

	or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #27:</u> Carbazones (Diazene carboxylic hydrazides), Bis(carbazones), and Poly(carbazones) (N-O Bidentates, N-O Tetridentates, and N-O Hexadentates)	R-N=N-C(=O)-NR'-N-R''R''' , where R, R', R'', and R''' represent H, or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #28:</u> Azo compounds including triazenes with hydroxyl or carboxy or carbonyl substitution at the ortho- (for aryl) or alpha- or beta- (for alkyl) positions, Bis[o-(HO-) or alpha- or beta-(HO-)azo compounds], or Poly[o-(HO-) or alpha- or beta-(HO-)azo compounds] (N-O Bidentates, N-O Tridentates, N-O Tetridentates, or N-O Hexadentates)	R-N=N-R' for azo compounds, R-N=N-NH-R' for triazenes, where R, and R' represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. (Must include ortho-hydroxy or carboxy or carbonyl substituted aryl azo compounds, and alpha- or beta-hydroxy or carboxy or carbonyl alkyl azo compounds.) Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #29:</u> Diazeneformamides, Diazeneacetamides, Bis(diazeneformamides), Bis(diazeneacetamides), Poly(diazeneformamides), and Poly(diazeneacetamides) (N-O Bidentates, N-O Tetridentates, and N-O Hexadentates)	R-N=N-C(=O)-NR'R'' for diazeneformamides, and R-N=N-CR'R''-C(=O)-NR'''R''' for diazeneacetamides, where R, R', R'', R''', and R''' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #30:</u> Diazeneformic acids, Diazeneacetic acids, Bis(diazeneformic acids), Bis(diazeneacetic acids), Poly(diazeneformic acids), Poly(diazeneacetic acids), and derivatives thereof (N-O Bidentates, N-O Tetridentates, N-O Hexadentates)	R-N=N-C(=O)-O-R' for diazeneformic acid, and R-N=N-CR'R''-C(=O)-O-R''' for diazeneacetic acid, where R, R', R'', and R''' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #31:</u> Diazeneformaldehydes,	R-N=N-C(=O)-R' for diazeneformaldehydes, and R-N=N-CR'R''-C(=O)-R''' for

Diazeneacetaldehydes, Bis(diazeneformaldehydes), Bis(diazeneacetaldehydes), Poly(diazeneformaldehydes), and Poly(diazeneacetaldehydes) (N-O Bidentates, N-O Tetridentates and N-O Hexadentates)	diazeneacetaldehydes, where R, R', R'', and R''' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #32:</u> Diazenediformamides, Diazenediacetamides, Bis(diazenediformamides), Bis(diazenediacetamides), Poly(diazenediformamides), and Poly(diazenediacetamides) (N-O Tridentates and N-O Hexadentates)	RR'-N-C(=O)-N=N-C(=O)-NR''R''' for diazenediformamides, and RR'-N-C(=O)-CR''R'''-N=N-CR''''R'''''-C(=O)-NR''''''R''''''' for diazenediacetamides, where R, R', R'', R''', R''''', R'''''', and R''''''' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #33:</u> Diazenediformic acids, Diazenediacetic acids, Bis(diazenediformic acids), Bis(diazenediacetic acids), Poly(diazenediformic acids), Poly(diazenediacetic acids) and derivatives thereof (N-O Tridentates and N-O Hexadentates)	R-O-C(=O)-N=N-C(=O)-O-R' for diazenediformic acid, and R-O-C(=O)-CR'R''-N=N-CR''''R'''''-C(=O)-O-R''''''' for diazenediacetic acid, where R, R', R'', R''', R''''', and R''''''' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #34:</u> Diazenediformaldehydes, Diazenediacetaldehydes, Bis(diazenediformaldehydes), Bis(diazenediacetaldehydes), Poly(diazenediformaldehydes), and Poly(diazenediacetaldehydes) (N-O Tridentates and N-O Hexadentates)	RC(=O)-N=N-C(=O)-R' for diazenediformaldehydes, and RC(=O)-CR'R''-N=N-CR''''R'''''-C(=O)-R''''''' for diazenediacetaldehydes, where R, R', R'', R''', R''''', and R''''''' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #35:</u> Ortho-hydroxy (or -carboxy) Substituted Formazans, Bis(o-hydroxy or -carboxy substituted formazans), and Poly(o-hydroxy or -carboxy substituted formazans) (N-O	R-N=N-CR'=N-NR''R''', where R, R', R'', and R''' represent H, or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-

Bidentates, N-O Tridentates, N-O Tetridentates, and N-O Hexadentates)	insolubilizing/solubilizing groups attached. (Must include ortho-hydroxy or carboxy substituted aryl R derivatives, and beta-hydroxy or carboxy substituted alkyl R derivatives.) Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #36:</u> Ortho-hydroxy (or -carboxy) Substituted Azines (including ketazines), Bis(o-hydroxy or carboxy substituted azines), and Poly(o-hydroxy or carboxy substituted azines) (N-O Bidentates, N-O Tridentates, N-O Tetridentates, and N-O Hexadentates)	RR'C=N-N=CR''R''' or RR'C=N-NR''R''' (for ketazines), where R, R', R'', and R''' represent H, or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. (Must include ortho-hydroxy or carboxy substituted aryl R derivatives, and beta-hydroxy or carboxy substituted alkyl R derivatives.) Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #37:</u> Schiff Bases with one Imine (C=N) Group and with ortho- or alpha- or beta-hydroxy or carboxy or carbonyl substitution (N-O Bidentates, N-O Tridentates, N-O Tetridentates, N-O Pentadentates, or N-O Hexadentates). Also includes hydrazones with ortho-O substitution.	RR'C=N-R'', where R, R', and R'' represent H, or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. (Must contain ortho- or alpha- or beta-hydroxy or carboxy or carbonyl substitution.) Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #38:</u> Schiff Bases with two Imine (C=N) Groups and with ortho- or alpha- or beta-hydroxy or carboxy or carbonyl substitution (N-O Tridentates, N-O Tetridentates, N-O Pentadentates, or N-O Hexadentates). Also includes hydrazones with ortho-O substitution.	RR'C=N-R''-N=CR'''R'''' or R-N=C-R'-C=N-R' or RC=N-R'-N=CR'', where R, R', R'', R''', and R'''' represent H, or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. (Must contain ortho- or alpha- or beta-hydroxy or carboxy or carbonyl substitution.) Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #39:</u> Schiff Bases with three Imine (C=N) Groups and with ortho- or alpha- or beta-hydroxy or carboxy or carbonyl substitution (N-O Tetridentates, N-O Pentadentates, or N-O Hexadentates). Also includes hydrazones with ortho-O substitution.	N(-R-N=CR'R'') ₃ , where R, R', and R'' represent H, or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. (Must contain ortho- or alpha- or beta-hydroxy or carboxy or carbonyl substitution.) Ligand can also contain nonbinding N, O, S, or P atoms.

<u>N-O Valence Stabilizer #40:</u> Silyl aminoalcohols (N-O Bidentates, N-O Tridentates, N-O Tetridentates, and N-O Hexadentates)	[R-C(NR'R'')] _x -R''-[Si(-OR'')] _z R''' _{3-z}] _y where R, R', R'', R''', and R'''' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached, and x and y = 1-6, z = 1-3. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #41:</u> Hydroxyalkyl Imines (Imino Alcohols) (N-O Bidentates, N-O Tridentates, N-O Tetridentates, and N-O Hexadentates)	[R-C(=NR')] _x -R''-[C(-OR'')]R'''R''''] _y or [R-C(=NR')] _x -R''-[C(=O)R'']] _y , where R, R', R'', R''', and R'''' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached, and x and y = 1-6. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #42:</u> Hydroxyaryl Amines and Hydroxyaryl Imines (N-O Bidentates, N-O Tridentates, N-O Tetridentates, and N-O Hexadentates)	[R(-NR'R'')(-OR'')], [R(-NR'R'')(-C(=O)R'')], [R(-NR'R'') _x] ₂ O, [R(-NR'R'') _x] ₂₋₃ R'''(-OR'')] _y , [R(-OR') _x] ₂ R''(-NR'''R'') _y , and [R(-NR'R'') _x] ₂ R'''(C(=O)) _y R'''' for hydroxyaryl amines; and [R(-OR') _x] ₂ NH or [R(-OR') _x] ₂ NHNH for hydroxyaryl imines, where R, R', R'', R''', and R'''' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached, and x = 0-2 and y = 1-4. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #43:</u> Five-Membered Heterocyclic Rings containing One, Two, Three, or Four Nitrogen Atoms at least one additional Oxygen Atom Binding Site not in a Ring (N-O Bidentates, N-O Tridentates, N-O Tetridentates, or N-O Hexadentates)	Five membered heterocyclic ring(s) containing one, two, three, or four nitrogen atoms. In addition, ligand contains additional oxygen-containing substituents (usually hydroxy, carboxy or carbonyl groups) that constitute O binding sites. Can include other ring systems bound to the heterocyclic ring or to the O-containing substituent, but they do not coordinate with the stabilized, high valence metal ion. Ring(s) can also contain O, S, or P atoms. This 5-membered ring(s) and/or attached, uncoordinating rings and/or O-containing substituent(s) may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>N-O Valence Stabilizer #44:</u>	Six membered heterocyclic ring(s) containing

<p>Six-Membered Heterocyclic Rings containing One, Two, Three, or Four Nitrogen Atoms at least one additional Oxygen Atom Binding Site not in a Ring (N-O Bidentates, N-O Tridentates, N-O Tetridentates, or N-O Hexadentates)</p>	<p>one, two, three, or four nitrogen atoms. In addition, ligand contains additional oxygen-containing substituents (usually hydroxy, carboxy, or carbonyl groups) that constitute O binding sites. Can include other ring systems bound to the heterocyclic ring or to the O-containing substituent, but they do not coordinate with the stabilized, high valence metal ion. Ring(s) can also contain O, S, or P atoms. This 6-membered ring(s) and/or attached, uncoordinating rings and/or O-containing substituent(s) may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.</p>
<p><u>N-O Valence Stabilizer #45:</u> Five-Membered Heterocyclic Rings containing One or Two Oxygen Atoms at least one additional Nitrogen Atom Binding Site not in a Ring (N-O Bidentates, N-O Tridentates, N-O Tetridentates, or N-O Hexadentates)</p>	<p>Five membered heterocyclic ring(s) containing one or two oxygen atoms. In addition, ligand contains additional nitrogen-containing substituents (usually amines, imines, or hydrazides) that constitute N binding sites. Can include other ring systems bound to the heterocyclic ring or to the N-containing substituent, but they do not coordinate with the stabilized, high valence metal ion. Ring(s) can also contain O, S, or P atoms. This 5-membered ring(s) and/or attached, uncoordinating rings and/or N-containing substituent(s) may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.</p>
<p><u>N-O Valence Stabilizer #46:</u> Six-Membered Heterocyclic Rings containing One or Two Oxygen Atoms at least one additional Nitrogen Atom Binding Site not in a Ring (N-O Bidentates, N-O Tridentates, N-O Tetridentates, or N-O Hexadentates)</p>	<p>Six membered heterocyclic ring(s) containing one or two oxygen atoms. In addition, ligand contains additional nitrogen-containing substituents (usually amines, imines, or hydrazides) that constitute N binding sites. Can include other ring systems bound to the heterocyclic ring or to the N-containing substituent, but they do not coordinate with the stabilized, high valence metal ion. Ring(s) can also contain O, S, or P atoms. This 6-membered ring(s) and/or attached, uncoordinating rings and/or N-containing substituent(s) may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.</p>
<p><u>N-O Valence Stabilizer #47:</u> Five-Membered Heterocyclic Rings containing One, Two, Three, or Four Nitrogen Atoms at least one additional</p>	<p>Five membered heterocyclic ring(s) containing one, two, three, or four nitrogen atoms. In addition, ligand contains additional oxygen-containing rings that constitute O binding sites.</p>

Oxygen Atom Binding Site in a Separate Ring (N-O Bidentates, N-O Tridentates, N-O Tetridentates)	Can include other ring systems bound to the N- or O-containing heterocyclic rings, but they do not coordinate with the stabilized, high valence metal ion. Ring(s) can also contain O, S, or P atoms. This 5-membered ring(s) and/or additional O-containing ring(s) and/or attached, uncoordinating rings may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>N-O Valence Stabilizer #48:</u> Six-Membered Heterocyclic Rings containing One, Two, Three, or Four Nitrogen Atoms at least one additional Oxygen Atom Binding Site in a Separate Ring (N-O Bidentates, N-O Tridentates, N-O Tetridentates)	Six membered heterocyclic ring(s) containing one, two, three, or four nitrogen atoms. In addition, ligand contains additional oxygen-containing rings that constitute O binding sites. Can include other ring systems bound to the N- or O-containing heterocyclic rings, but they do not coordinate with the stabilized, high valence metal ion. Ring(s) can also contain O, S, or P atoms. This 6-membered ring(s) and/or additional O-containing ring(s) and/or attached, uncoordinating rings may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>N-O Valence Stabilizer #49:</u> Two-, Three-, Four-, Six-, Eight-, and Ten-Membered Macrocyclics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Nitrogen (usually amine or imine groups) or Oxygen (usually hydroxy, carboxy, or carbonyl groupss) and are not contained in Component Heterocyclic Rings (N-O Bidentates, N-O Tridentates, N-O Tetridentates, and N-O Hexadentates)	Macrocyclic ligands containing two, three, four, six, eight, or ten binding sites composed of nitrogen and oxygen to valence stabilize the central metal ion. Can include other hydrocarbon or ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbons/rings may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>N-O Valence Stabilizer #50:</u> Four-, Six-, Eight-, or Ten-Membered Macrocyclics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Nitrogen or Oxygen and are contained in Component Heterocyclic Rings (N-O Bidentates, N-O Tridentates, N-O Tetridentates, or N-O Hexadentates)	Macrocyclic ligands containing a total of four, six, eight, or ten heterocyclic rings containing nitrogen or oxygen binding sites. Can include other hydrocarbon/ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbon/rings may or may not have halogen or polarizing or water-insolubilizing groups attached.
<u>N-O Valence Stabilizer #51:</u> Four-, Six-, Eight-, or Ten-Membered	Macrocyclic ligands containing at least one heterocyclic ring. These heterocyclic rings

<p>Macrocyclics, Macroyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Nitrogen or Oxygen and are contained in a Combination of Heterocyclic Rings and Amine, Imine, Hydroxy, Carboxy, or Carbonyl Groups (N-O Bidentates, N-O Tridentates, N-O Tetridentates, or N-O Hexadentates)</p>	<p>provide nitrogen or oxygen binding sites to valence stabilize the central metal ion. Other amine, imine, hydroxy, carboxy, or carbonyl binding sites can also be included in the macrocyclic ligand, so long as the total number of binding sites is four, six, eight, or ten. Can include other hydrocarbon/ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbon/rings may or may not have halogen or polarizing or water-insolubilizing groups attached.</p>
<p>S-O Valence Stabilizer #1: 1,3-Monothioketones (Monothio-beta-ketonates), 1,3,5-Monothioketones, 1,3,5-Dithioketones, Bis(1,3-Monothioketones), and Poly(1,3-Monothioketones) (S-O Bidentates, S-O Tridentates, S-O Tetridentates)</p>	<p>R-C(=S)-CR'R"-C(=O)-R''' where R, R', R'', and R''' represent H, NH₂, or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.</p>
<p>S-O Valence Stabilizer #2: Thiomalonamides (Thiomalonodiamides), Bis(thiomalonamides), and Polythiomalonamides (S-O Bidentates, S-O Tridentates, S-O Tetridentates)</p>	<p>RR'-N-C(=S)-CR''R'''-C(=O)-N-R''''R''''' where R, R', R'', R''', R''''', and R''''' represent H, NH₂, or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.</p>
<p>S-O Valence Stabilizer #3: 2-Thioacylacetamides, 2-Acylthioacetamides, Bis(2-thioacylacetamides), Bis(2acylthioacetamides), Poly(2-thioacylacetamides), and Poly(2-Acylthioacetamides) (S-O Bidentates, S-O Tridentates, S-O Tetridentates)</p>	<p>RR'-N-C(=O)-CR''R'''-C(=S)-R''''' for 2-thioacylacetamides, and RR'-N-C(=S)-CR''R'''-C(=O)-R''''' for 2-acylthioacetamides, where R, R', R'', R''', and R''''' represent H, NH₂, or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.</p>
<p>S-O Valence Stabilizer #4: Dithiodicarbonic Diamides, Bis(dithiodicarbonic diamides), and Poly(dithiodicarbonic diamides) (S-O Bidentates, S-O Tridentates, S-O Tetridentates)</p>	<p>RR'-N-C(=S)-S-C(=O)-N-R''R''''' where R, R', R'', and R''''' represent H, NH₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or</p>

<u>S-O Valence Stabilizer #5:</u> Monothiohypophosphoric Acids, Bis(monothiohypophosphoric acids), and Poly(monothiohypophosphoric acids), and derivatives thereof (S-O Bidentates, S-O Tridentates, S-O Tetridentates)	P atoms. (R-O-)(R'-O-)P(=S)-P(=O)(-O-R'')(-O-R'''); (R-O-)(R'-S-)P(=S)-P(=O)(-S-R'')(-O-R'''); or (R-S-)(R'-S-)P(=S)-P(=O)(-S-R'')(-S-R'''), where R, R', R'', and R''' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms. Note: these ligands are not to be confused with hypophosphorous acid derivatives (hypophosphites) (R-O-)R''R'''P(=O) which are very reducing and therefore unacceptable for stabilization of high valence states in metal ions.
<u>S-O Valence Stabilizer #6:</u> Monothiohypophosphoramides, Bis(monothiohypophosphoramides), and Poly(monothiohypophosphoramides) (S-O Bidentates, S-O Tridentates, S-O Tetridentates)	(RR'-N-)(R''R''''-N-)P(=S)-P(=O)(-N- R''''R''''')(-N-R''''''R'''''''), where R, R', R'', R''', R''''', R'''''', R''''''', and R''''''''' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms. Note: these ligands are not to be confused with hypophosphorous acid derivatives (hypophosphites) (R-O-)R''R'''P(=O) which are very reducing and therefore unacceptable for stabilization of high valence states in metal ions.
<u>S-O Valence Stabilizer #7:</u> Monothioimidodiphosphoric Acids, Monothiohydrazidodiphosphoric Acids, Bis(monothioimidodiphosphoric Acids), Bis(monothiohydrazidodiphosphoric Acids), Poly(monothioimidodiphosphoric Acid), Poly(monothiohydrazidodiphosphoric Acids), and derivatives thereof (S-O Bidentates, S-O Tridentates, S-O Tetridentates)	(R-O-)(R'-O-)P(=S)-NH-P(=O)(-O-R'')(-O- R'''); (R-O-)(R'-S-)P(=S)-NH-P(=O)(-S-R'')(- O-R'''); or (R-S-)(R'-S-)P(=S)-NH-P(=O)(-S- R'')(-S-R''') for monothioimidodiphosphoric acids, and -NH-NH- derivatives for monothiohydrazidodiphosphoric acids, where R, R', R'', and R''' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water- insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S-O Valence Stabilizer #8:</u> Monothioimidodiphosphoramides, Monothiohydrazidodiphosphoramides,	(RR'-N-)(R''R''''-N-)P(=S)-NH-P(=O)(-N- R''''R''''')(-N-R''''''R''''''') for monothioimidodiphosphoramides, and -NH-

<p>Bis(monothioimidodiphosphoramides), Bis(monothiohydrazidodiphosphoramides), Poly(monothioimidodiphosphoramides), and Poly(monothiohydrazidodiphosphoramides) (S-O Bidentates, S-O Tridentates, S-O Tetridentates)</p>	<p>NH- derivatives for monothiohydrazidodiphosphoramides, where R, R', R'', R''', R'''', R''''', and R''''' represent H, NH₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.</p>
<p><u>S-O Valence Stabilizer #9:</u> Monothiodiphosphoramides, Bis(monothioiphosphoramides), and Poly(monothiodiphosphoramides) (S-O Bidentates, S-O Tridentates, S-O Tetridentates)</p>	<p>(RR'-N-)(R''R'''-N-)P(=S)-S-P(=O)(-N-R''''R''''')(-N-R''''''R'''''''), or (RR'-N-)(R''R'''-N-)P(=S)-O-P(=O)(-N-R''''R''''')(-N-R''''''R'''''''), where R, R', R'', R''', R''''', R''''''', and R''''' represent H, NH₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.</p>
<p><u>S-O Valence Stabilizer #10:</u> Monothiodiphosphoric Acids, Bis(monothioiphosphoric Acids), Poly(monothiodiphosphoric Acids), and derivatives thereof (S-O Bidentates, S-O Tridentates, S-O Tetridentates)</p>	<p>(R-O-)(R'-O-)P(=S)-O-P(=O)(-O-R'')(-O-R'''); (R-O-)(R'-O-)P(=S)-S-P(=O)(-O-R'')(-O-R'''); (R-O-)(R'-S-)P(=S)-O-P(=O)(-S-R'')(-O-R'''); (R-O-)(R'-S-)P(=S)-S-P(=O)(-S-R'')(-O-R'''); or (R-S-)(R'-S-)P(=S)-S-P(=O)(-S-R'')(-S-R'''), where R, R', R'', R''', R''''', R'''''', and R''''' represent H, NH₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.</p>
<p><u>S-O Valence Stabilizer #11:</u> Monothiocarbamates, Bis(monothiocarbamates), and Poly(monothiocarbamates) (including N-hydroxymonothiocarbamates and N-mercaptomonothiocarbamates) (S-O Bidentates, S-O Tridentates, and S-O Tetridentates)</p>	<p>RR'N⁺=C(OH)(SH), where R and R' represent H, OH, SH, OR'' (R''=C₁-C₃₀ alkyl or aryl), SR'' (R''=C₁-C₃₀ alkyl or aryl), NH₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.</p>

N Valence Stabilizer #1: Examples of monoamines (N monodentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: ammonia, ethylamine, n-dodecylamine, octylamine, phenylamine, cyclohexylamine, diethylamine, dioctylamine, diphenylamine, dicyclohexylamine, azetidine, hexamethylenetetramine, aziridine, 5 azepine, pyrrolidine, benzopyrrolidine, dibenzopyrrolidine, naphthopyrrolidine, piperidine, benzopiperidine, dibenzopiperidine, naphthopiperidine, azacycloheptane (hexamethyleneimine (Urotropin)), aminonorbornane, adamantanamine, aniline, benzylamine, toluidine, phenethylamine, xylidine, cumidine, naphthylamine, polyalkylamines, polyanilines, and fluorenediamine.

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N Valence Stabilizer #2: Examples of diamines (N-N bidentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: hydrazine, phenylhydrazine, 1,1-diphenylhydrazine, 1,2-diphenylhydrazine (hydrazobenzene), methanediamine, ethylenediamine (1,2-ethanediamine, en), trimethylenediamine (1,3-propanediamine), putrescine (1,4-butanediamine), cadaverine (1,5-pentanediamine), hexamethylenediamine (1,6-hexanediamine), 2,3-diaminobutane, stilbenediamine (1,2-diphenyl-1,2-ethanediamine), cyclohexane-1,2-diamine, cyclopentane-1,2-diamine, 1,3-diazacyclopentane, 1,3-diazacyclohexane, piperazine, benzopiperazine, dibenzopiperazine, naphthopiperazine, diazepine, thiadiazepine, oxodiazepine, sparteine (lupinidine), 2-(aminomethyl)azacyclohexane, 2-(aminomethyl)piperidine, 2-(aminomethyl)pyrrolidine, 2-(aminomethyl)azetidine, 2-(2-aminoethyl)aziridine, 1,2-diaminobenzene, benzidine, bis(2,2'-piperazino)-1,2-ethene, 1,4-diazabicyclo[2.2.2]octane, naphthylethylenediamine, and 1,2-dianilinoethane.

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N Valence Stabilizer #3: Examples of triamines (N-N bidentates or N-N tridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: N-(2-aminoethyl)-1,2-ethanediamine (dien, 2,2-tri); N-(2-aminoethyl)-1,3-propanediamine (2,3-tri); N-(3aminopropyl)-1,3-propanediamine (3,3-tri, dpt); N-(3-aminopropyl)-1,4-butanediamine (3,4-tri, spermidine); N-(2-aminoethyl)-1,4-butanediamine (2,4-tri); N-(6-hexyl)-1,6-hexanediamine (6,6-tri); 1,3,5-triaminocyclohexane (tach); 2-(aminomethyl)-1,3-propanediamine (tamm); 2-(aminomethyl)-2-methyl-1,3-propanediamine (tame); 2-

(aminomethyl)-2-ethyl-1,3-propanediamine (tamp); 1,2,3-triaminopropane (tap); 2,3-(2-aminoethyl)aziridine; 2,4-(aminomethyl)azetidine; 2,5-(aminomethyl)pyrrolidine; 2,6-(aminomethyl)piperidine; di(2-aminobenzyl)amine; hexahydro-1,3,5-triazine; hexahydro-2,4,6-trimethyl-1,3,5-triazine; and 1,3,5-tris(aminomethyl)benzene.

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N Valence Stabilizer #4: Examples of tetramines (N-N bidentates, N-N tridentates, or N-N tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: N,N’-(2-aminoethyl)-1,2-ethanediamine (2,2,2-tet, trien (triethylenetetramine)); N,N’-(2-aminoethyl)-1,3-propanediamine (2,3,2-tet, entnen); N,N’-(3-aminopropyl)-1,2-ethanediamine (3,2,3-tet, tnentn); N-(2-aminoethyl)-N’-(3-aminopropyl)-1,2-ethanediamine (2,2,3-tet); N-(2-aminoethyl)-N’-(3-aminopropyl)-1,3-propanediamine (3,3,2-tet); N,N’-(3-aminopropyl)-1,3-propanediamine (3,3,3-tet); N,N’-(3-aminopropyl)-1,4-butanediamine (3,4,3-tet, spermine); tri(aminomethyl)amine (tren); tri(2-aminoethyl)amine (trtn); tri(3-aminopropyl)amine (trbn); 2,2-aminomethyl-1,3-propanediamine (tam); 1,2,3,4-tetraaminobutane (tab); N,N’-(2-aminophenyl)-1,2-ethanediamine; and N,N’-(2-aminophenyl)-1,3-propanediamine.

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N Valence Stabilizer #5: Examples of pentamines (N-N bidentates, N-N tridentates, or N-N tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: N-[N-(2-aminoethyl)-2-aminoethyl]-N’-(2-aminoethyl)-1,2-ethanediamine (2,2,2,2-pent, tetren); N-[N-(3-aminopropyl)-2-aminoethyl]-N’-(3-aminopropyl)-1,2-ethanediamine (3,2,2,3-pent); N-[N-(3-aminopropyl)-3-aminopropyl]-N’-(3-aminopropyl)-1,3-propanediamine (3,3,3,3-pent, caldopentamine); N-[N-(2-aminobenzyl)-2-aminoethyl]-N’-(2-aminopropyl)-1,2-ethanediamine; N-[N-(2-aminoethyl)-2-aminoethyl]-N,N-(2-aminoethyl)amine (trenen); and N-[N-(2-aminopropyl)-2-aminoethyl]-N,N-(2-aminoethyl)amine (4-Me-trenen).

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N Valence Stabilizer #6: Examples of hexamines (N-N bidentates, N-N tridentates, N-N tetridentates, or N-N-N-N-N-N hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: N,N’-[N-(2-aminoethyl)-2-aminoethyl]-1,2-ethanediamine (2,2,2,2,2-hex, linpen); N,N’-[N-(2-aminoethyl)-3-aminopropyl]-

1,2-ethanediamine (2,3,2,3,2-hex); N,N,N',N'-(2-aminoethyl)-1,2-ethanediamine (penten, ten);
N,N,N',N'-(2-aminoethyl)-1-methyl-1,2-ethanediamine (tpn, R-5-Me-penten); N,N,N',N'-(2-
aminoethyl)-1,3-propanediamine (ttn); N,N,N',N'-(2-aminoethyl)-1,4-butanediamine (tbn);
N,N,N',N'-(2-aminoethyl)-1,3-dimethyl-1,3-propanediamine (R,R-tptn, R,S-tptn); N-(2-
aminoethyl)-2,2-[N-(2-aminoethyl)aminomethyl-1-propaneamine (sen); and N-(3-aminopropyl)-
2,2-[N-(3-aminopropyl)aminomethyl-1-propaneamine (stn).

5 N Valence Stabilizer #7a: Examples of 5-membered heterocyclic rings containing one nitrogen
atom (N monodentates) that meet the requirements for use as “wide band” valence stabilizers for
Ce⁺⁴ include, but are not limited to: 1-pyrroline, 2-pyrroline, 3-pyrroline, pyrrole, oxazole,
10 isoxazole, thiazole, isothiazole, azaphosphole, benzopyrroline, benzopyrrole (indole),
benzoxazole, benzisoxazole, benzothiazole, benzisothiazole, benzazaphosphole,
dibenzopyrroline, dibenzopyrrole (carbazole), dibenzoxazole, dibenzisoxazole, dibenzothiazole,
15 dibenzisothiazole, naphthopyrroline, naphthopyrrole, naphthoxazole, naphthisoxazole,
naphthothiazole, naphthisothiazole, naphthazaphosphole, and polypyrrroles.

20 N Valence Stabilizer #7b: Examples of 5-membered heterocyclic rings containing two nitrogen
atoms (N monodentates or N-N bidentates) that meet the requirements for use as “wide band”
valence stabilizers for Ce⁺⁴ include, but are not limited to: pyrazoline, imidazoline, imidazole
(ia), pyrazole, oxadiazole, thiadiazole, diazaphosphole, benzopyrazoline, benzimidazoline,
benzimidazole (azindole)(bia)(bz), benzopyrazole (indazole), benzothiadiazole (piazthiole),
benzoxadiazole (benzfurazan), naphthopyrazoline, naphthimidazoline, naphthimidazole,
naphthopyrazole, naphthoxadiazole, naphthothiadiazole, polybenzimidazole, and polyimidazoles
(e.g. polyvinylimidazole (pvi)).

25 N Valence Stabilizer #7c: Examples of 5-membered heterocyclic rings containing three nitrogen
atoms (N monodentates, N-N bidentates) that meet the requirements for use as “wide band”
valence stabilizers for Ce⁺⁴ include, but are not limited to: triazole, oxatriazole, thiatriazole,
benzotriazole (bta), tolyltriazole (tt), naphthotriazole, and triazolophthalazine.

N Valence Stabilizer #7d: Examples of 5-membered heterocyclic rings containing four nitrogen atoms (N monodentates or N-N bidentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: tetrazole.

5 N Valence Stabilizer #8a: Examples of 6-membered heterocyclic rings containing one nitrogen atom (N monodentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: pyridine, picoline, lutidine, -collidine, oxazine, thiazine, azaphosphorin, quinoline, isoquinoline, benzoxazine, benzothiazine, benzazaphosphorin, acridine, phenanthridine, phenothiazine (dibenzothiazine), dibenzoxazine, dibenzazaphosphorin, 10 benzoquinoline (naphthopyridine), naphthoxazine, naphthothiazine, naphthazaphosphorin, and polypyridines.

15 N Valence Stabilizer #8b: Examples of 6-membered heterocyclic rings containing two nitrogen atoms (N monodentates or N-N bidentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: pyrazine, pyridazine, pyrimidine, oxadiazine, thiadiazine, diazaphosphorin, quinoxaline (benzopyrazine), cinnoline (benzo[c]pyridazine), quinazoline (benzopyrimidine), phthalazine (benzo[d]pyridazine), benzoxadiazine, benzothiadiazine, phenazine (dibenzopyrazine), dibenzopyridazine, naphthopyrazine, naphthopyridazine, naphthopyrimidine, naphthoxadiazine, naphthothiadiazine, 20 and polyquinoxalines.

25 N Valence Stabilizer #8c: Examples of 6-membered heterocyclic rings containing three nitrogen atoms (N monodentates or N-N bidentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 1,3,5-triazine, 1,2,3-triazine, benzo-1,2,3-triazine, naphtho-1,2,3-triazine, oxatriazine, thiatriazine, melamine, and cyanuric acid.

30 N Valence Stabilizer #8d: Examples of 6-membered heterocyclic rings containing four nitrogen atoms (N monodentates or N-N bidentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: tetrazine.

N Valence Stabilizer #9a: Examples of 5-membered heterocyclic rings containing one nitrogen atom and having at least one additional nitrogen atom binding site not contained in a ring (N Monodentates, N-N Bidentates, N-N Tridentates, N-N Tetridentates, or N-N Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-(aminomethyl)-3-pyrroline; 2,5-(aminomethyl)-3-pyrroline; 2-(aminomethyl)pyrrole; 2,5-(aminomethyl)pyrrole; 3-(aminomethyl)isoxazole; 2-(aminomethyl)thiazole; 3-(aminomethyl)isothiazole; 2-(aminomethyl)indole; 2-aminobenzoxazole; 2-aminobenzothiazole (abt); 1,8-diaminocarbazole; 2-amino-6-methylbenzothiazole (amebt); 2-amino-6-methoxybenzothiazole (ameobt); and 1,3-diiminoisoindoline.

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N Valence Stabilizer #9b: Examples of 5-membered heterocyclic rings containing two nitrogen atoms at least one additional nitrogen atom binding site not contained in a ring (N Monodentates, N-N Bidentates, N-N Tridentates, N-N Tetridentates, or N-N Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to:

15 2-aminoimidazoline; 1-(3-aminopropyl)imidazoline; 2-aminoimidazole; 1-(3-aminopropyl)imidazole; 4-(2-aminoethyl)imidazole [histamine]; 1-alkyl-4-(2-aminoethyl)imidazole; 3-(2-aminoethyl)pyrazole; 3,5-(2-aminoethyl)pyrazole; 1-(aminomethyl)pyrazole; 2-aminobenzimidazole; 7-(2-aminoethyl)benzimidazole; 1-(3-aminopropyl)benzimidazole; 3-(2-aminoethyl)indazole; 3,7-(2-aminoethyl)indazole; 1-(aminomethyl)indazole; 7-aminobenzothiadiazole; 4-(2-aminoethyl)benzothiadiazole; 7-aminobenzoxadiazole; 4-(2-aminoethyl)benzoxadiazole; ethylenediaminetetra(1-pyrazolylmethane) [edtp]; methylenenitrilotris(2-(1-methyl)benzimidazole) [mntb] [tris(1-methyl-2-benzimidazolylmethane)amine]; bis(alkyl-1-pyrazolylmethane)amine; bis(alkyl-2-(1-pyrazolyl)ethane)amine; bis(N,N-(2-benzimidazolyl)-2-aminoethane)(2-benzimidazolylmethane)amine; bis(1-(3,5-dimethyl)pyrazolylmethane)phenylamine; tris(2-(1-(3,5-dimethyl)pyrazolyl)ethane)amine; 5-(dimethylamino)pyrazole; 5-(dimethylaminomethyl)pyrazole; 2-amino-1,3,4-thiadiazole; and 1-(2-aminoethyl)imidazoline.

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30 N Valence Stabilizer #9c: Examples of 5-membered heterocyclic rings containing three nitrogen atoms at least one additional nitrogen atom binding site not contained in a ring (N Monodentates, N-N Bidentates, N-N-N Tridentates, N-N-N-N Tetridentates, or N-N-N-N-N Hexadentates)

that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 3-amino-1,2,4-triazole (ata); 3,5-diamino-1,2,4-triazole (dat); 5-amino-1,2,4-triazole; 3-(2-aminoethyl)-1,2,4-triazole; 5-(2-aminoethyl)-1,2,4-triazole; 3,5-(2-aminoethyl)-1,2,4-triazole; 1-(aminomethyl)-1,2,4-triazole; 3,5-(aminomethyl)-4-amino-1,2,4-triazole; 4-(2-aminoethyl)-1,2,3-triazole; 5-(2-aminoethyl)-1,2,3-triazole; 7-aminobenzotriazole; 1-(aminomethyl)-1,2,3-triazole; 1-(2-aminoethyl)-1,2,3-triazole; 4-(3-aminopropyl)benzotriazole; N-(benzotriazolylalkyl)amine; dibenzotriazole-1-ylalkylamine; bis(5-amino-1,2,4-triazol-3-yl); bis(5-amino-1,2,4-triazol-3-yl)alkanes; and 1-(aminomethyl)benzotriazole.

10 N Valence Stabilizer #9d: Examples of 5-membered heterocyclic rings containing four nitrogen atoms at least one additional nitrogen atom binding site not contained in a ring (N Monodentates, N-N Bidentates, N-N Tridentates, N-N Tetridentates, or N-N Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 5-(2-aminoethyl)-1H-tetrazole; 1-(aminomethyl)-1H-tetrazole; and 1-(2-aminoethyl)-1H-tetrazole.

15 N Valence Stabilizer #10a: Examples of 6-membered heterocyclic rings containing one nitrogen atom and having at least one additional nitrogen atom binding site not contained in a ring (N Monodentates, N-N Bidentates, N-N Tridentates, N-N Tetridentates, or N-N Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-aminopyridine; 2,6-diaminopyridine; 2-(aminomethyl)pyridine; 2,6-(aminomethyl)pyridine; 2,6-(aminoethyl)pyridine; 2-amino-4-picoline; 2,6-diamino-4-picoline; 2-amino-3,5-lutidine; 2-aminoquinoline; 8-aminoquinoline; 2-aminoisoquinoline; acriflavine; 4-aminophenanthridine; 4,5-(aminomethyl)phenothiazine; 4,5-(aminomethyl)dibenzoxazine; 10-amino-7,8-benzoquinoline; bis(2-pyridylmethane)amine; tris(2-pyridyl)amine; bis(4-(2-pyridyl)-3-azabutane)amine; bis(N,N-(2-(2-pyridyl)ethane)aminomethane)amine; 4-(N,N-dialkylaminomethyl)morpholine; 6-aminonicotinic acid; 8-aminoacridine; and 2-hydrazinopyridine.

20 N Valence Stabilizer #10b: Examples of 6-membered heterocyclic rings containing two nitrogen atoms at least one additional nitrogen atom binding site not contained in a ring (N Monodentates,

N-N Bidentates, N-N Tridentates, N-N Tetridentates, or N-N Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-aminopyrazine; 2,6-diaminopyrazine; 2-(aminomethyl)pyrazine; 2,6-(aminomethyl)pyrazine; 3-(aminomethyl)pyridazine; 3,6-(aminomethyl)pyridazine; 3,6-(2-aminoethyl)pyridazine; 1-aminopyridazine; 1-(aminomethyl)pyridazine; 2-aminopyrimidine; 1-(2-aminoethyl)pyrimidine; 2-aminoquinoxaline; 2,3-diaminoquinoxaline; 2-aminocinnoline; 3-aminocinnoline; 3-(2-aminoethyl)cinnoline; 3,8-(2-aminoethyl)cinnoline; 2-aminoquinazoline; 1-(2-aminoethyl)quinazoline; 1-aminophthalazine; 1,4-(2-aminoethyl)phthalazine; 1,8-(aminomethyl)phenazine;

10 2-amino-4,6-dimethylpyrimidine (admp); dihydralazine; and hydralazine.

N Valence Stabilizer #10c: Examples of 6-membered heterocyclic rings containing three nitrogen atoms at least one additional nitrogen atom binding site not contained in a ring (N Monodentates, N-N Bidentates, N-N Tridentates, N-N Tetridentates, or N-N Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-amino-1,3,5-triazine; 2-(aminomethyl)-1,3,5-triazine; 2,6-(aminomethyl)-1,3,5-triazine; 1-(3-aminopropyl)-1,3,5-triazine; 1,5-(3-aminopropyl)-1,3,5-triazine; polymelamines; melamine; and altretamine.

20 N Valence Stabilizer #10d: Examples of 6-membered heterocyclic rings containing four nitrogen atoms at least one additional nitrogen atom binding site not contained in a ring (N Monodentates, N-N Bidentates, N-N Tridentates, N-N Tetridentates, or N-N Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 3,6-(2-aminoethyl)-1,2,4,5-tetrazine; 3,6-(1,3-diamino-2-propyl)-1,2,4,5-tetrazine; and 4,6-(aminomethyl)-1,2,3,5-tetrazine.

25 N Valence Stabilizer #11a: Examples of 5-membered heterocyclic rings containing one nitrogen atom and having at least one additional nitrogen atom binding site contained in a ring (N Monodentates, N-N Bidentates, N-N Tridentates, N-N Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2,2'-bi-3-pyrroline; 2,2'-bi-2-pyrroline; 2,2'-bi-1-pyrroline; 2,2'-bipyrrole; 2,2',2"-tripyrrrole; 3,3'-

biisoxazole; 2,2'-bioxazole; 3,3'-biisothiazole; 2,2'-bithiazole; 2,2'-biindole; 2,2'-bibenzoxazazole; 2,2'-bibenzothiazole; bilirubin; biliverdine; and 7-azaindole.

N Valence Stabilizer #11b: Examples of 5-membered heterocyclic rings containing two nitrogen atoms at least one additional nitrogen atom binding site contained in a ring (N Monodentates, N-N Bidentates, N-N Tridentates, N-N Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2,2'-bi-2-imidazoline [2,2'-bi-2-imidazolinyl] [bimd]; 2,2'-biimidazole [2,2'-biimidazolyl] [biimH₂]; 5,5'-bipyrazole; 3,3'-bipyrazole; 4,4'-bipyrazole [4,4'-bipyrazolyl] [bpz]; 2,2'-bioxadiazole; 2,2'-bithiadiazole; 2,2'-bibenzimidazole; 7,7'-biindazole; 5,5'-bibenzofurazan; 5,5'-bibenzothiadiazole; bis-1,2-(2-benzimidazole)ethane; bis(2-benzimidazole)methane; 1,2-(2-imidazolyl)benzene; 2-(2-thiazolyl)benzimidazole; 2-(2-imidazolyl)benzimidazole; benzimidazotriazine; 4-azabenzimidazole; and 2,6-bis(2-benzimidazolyl)pyridine.

N Valence Stabilizer #11c: Examples of 5-membered heterocyclic rings containing three nitrogen atoms at least one additional nitrogen atom binding site contained in a ring (N Monodentates, N-N Bidentates, N-N Tridentates, N-N Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 5,5'-bi-1,2,4-triazole [btrz]; 3,3'-bi-1,2,4-triazole; 1,1'-bi-1,2,4-triazole; 1,1'-bi-1,2,3-triazole; 5,5'-bi-1,2,3-triazole; 7,7'-bibenzotriazole; 1,1'-bibenzotriazole; bis(pyridyl)aminotriazole (pat); and 8-azaadenine.

N Valence Stabilizer #11d: Examples of 5-membered heterocyclic rings containing four nitrogen atoms at least one additional nitrogen atom binding site contained in a ring (N Monodentates, N-N Bidentates, N-N Tridentates, N-N Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 5,5'-bi-1H-tetrazole; and 1,1'-bi-1H-tetrazole.

N Valence Stabilizer #12a: Examples of 6-membered heterocyclic rings containing one nitrogen atom and having at least one additional nitrogen atom binding site contained in a ring (N Monodentates, N-N Bidentates, N-N Tridentates, N-N Tetridentates) that meet the requirements

for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2,2'-bipyridine [bipy]; 2,2',2"-tripyridine [terpyridine] [terpy]; 2,2',2",2""-tetrapyridine [tetrapy]; 6,6'-bi-2-picoline; 6,6'-bi-3-picoline; 6,6'-bi-4-picoline; 6,6'-bi-2,3-lutidine; 6,6'-bi-2,4-lutidine; 6,6'-bi-3,4-lutidine; 6,6'-bi-2,3,4-collidine; 2,2'-biquinoline; 2,2'-biisoquinoline; 3,3'-bibenzoxazine; 5 3,3'-bibenzothiazine; 1,10-phenanthroline [phen]; 1,8-naphthyridine; bis-1,2-(6-(2,2'-bipyridyl))ethane; bis-1,3-(6-(2,2'-bipyridyl))propane; 3,5-bis(3-pyridyl)pyrazole; 3,5-bis(2-pyridyl)triazole; 1,3-bis(2-pyridyl)-1,3,5-triazine; 1,3-bis(2-pyridyl)-5-(3-pyridyl)-1,3,5-triazine; 2,7-(N,N'-di-2-pyridyl)diaminobenzopyrroline; 2,7-(N,N'-di-2-pyridyl)diaminophthalazine; 2,6-di-(2-benzothiazolyl)pyridine; triazolopyrimidine; 2-(2-pyridyl)imidazoline; 7-azaindole; 1-(2-pyridyl)pyrazole; (1-imidazolyl)(2-pyridyl)methane; 4,5-bis(N,N'-(2-(2-pyridyl)ethyl)iminomethyl)imidazole; bathophenanthroline; 4-(2-benzimidazolyl)quinoline; 1,2-bis(2-pyridyl)ethane; 4,4'-diphenyl-2,2'-dipyridyl; neocuproine; nicotine; and nornicotine.

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15 N Valence Stabilizer #12b: Examples of 6-membered heterocyclic rings containing two nitrogen atoms at least one additional nitrogen atom binding site contained in a ring (N Monodentates, N-N Bidentates, N-N Tridentates, N-N Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2,2'-bipyrazine; 2,2',2"-tripyrazine; 6,6'-bipyridazine; bis(3-pyridazinyl)methane; 1,2-bis(3-pyridazinyl)ethane; 2,2'-bipyrimidine; 2,2'-biquinoxaline; 8,8'-biquinoxaline; bis(3-cinnolinyl)methane; bis(3-cinnolinyl)ethane; 8,8'-bicinnoline; 2,2'-biquinazoline; 4,4'-biquinazoline; 8,8'-biquinazoline; 2,2'-biphthalazine; 1,1'-biphthalazine; 2-(2-pyridyl)benzimidazole; 8-azapurine; purine; adenine; guanine; hypoxanthine; 2,6-bis(N,N'-(2-(4-imidazolyl)ethyl)iminomethyl)pyridine; 2-(N-(2-(4-imidazolyl)ethyl)iminomethyl)pyridine; adenine (aminopurine); purine; and 2,3-bis(2-pyridyl)pyrazine.

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25 N Valence Stabilizer #12c: Examples of 6-membered heterocyclic rings containing three nitrogen atoms at least one additional nitrogen atom binding site contained in a ring (N Monodentates, N-N Bidentates, N-N Tridentates, N-N Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2,2'-bi-1,3,5-triazine; 2,2',2"-tri-1,3,5-triazine; 4,4'-bi-1,2,3-triazine; and 4,4'-bibenzo-1,2,3-triazine; 2,4,6-tris(2-pyridyl)-1,3,5-triazine; and benzimidazotriazines.

N Valence Stabilizer #12d: Examples of 6-membered heterocyclic rings containing four nitrogen atoms at least one additional nitrogen atom binding site contained in a ring (N Monodentates, N-N Bidentates, N-N Tridentates, N-N Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 3,3’-bi-1,2,4,5-tetrazine; and
5 4,4’-bi-1,2,3,5-tetrazine.

N Valence Stabilizer #13a: Examples of two-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein both binding sites are composed of nitrogen (usually amine or imine groups) and are not contained in
10 component heterocyclic rings (N-N Bidentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diazacyclobutane ([4]aneN₂); diazacyclopentane ([5]aneN₂); diazacyclohexane ([6]aneN₂); diazacycloheptane ([7]aneN₂); diazacyclooctane ([8]aneN₂); piperazine; benzopiperazine; diazacyclobutene ([4]eneN₂); diazacyclopentene ([5]eneN₂); diazacyclohexene ([6]eneN₂); diazacycloheptene ([7]eneN₂);
15 diazacyclooctene ([8]eneN₂); diazacyclobutadiene ([4]dieneN₂); diazacyclopentadiene ([5]dieneN₂); diazacyclohexadiene ([6]dieneN₂); diazacycloheptadiene ([7]dieneN₂); and diazacyclooctadiene ([8]dieneN₂).

N Valence Stabilizer #13b: Examples of three-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of nitrogen (usually amine or imine groups) and are not contained in component heterocyclic rings (N-N Tridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: triazacyclohexane (including hexahydro-1,3,5-triazine)([6]aneN₃); triazacycloheptane ([7]aneN₃); triazacyclooctane ([8]aneN₃); triazacyclononane ([9]aneN₃); triazacyclodecane ([10]aneN₃); triazacycloundecane ([11]aneN₃); triazacyclododecane ([12]aneN₃); triazacyclohexene ([6]eneN₃); triazacycloheptene ([7]eneN₃); triazacyclooctene ([8]eneN₃); triazacyclononene ([9]eneN₃); triazacyclodecene ([10]eneN₃); triazacycloundecene ([11]eneN₃); triazacyclododecene ([12]eneN₃); triazacyclohexatriene ([6]trieneN₃); triazacycloheptatriene ([7]trieneN₃); triazacyclooctatriene ([8]trieneN₃); triazacyclononatriene ([9]trieneN₃); triazacyclodecatriene ([10]trieneN₃); triazacycloundecatriene ([11]trieneN₃); and triazacyclododecatriene ([12]trieneN₃).

N Valence Stabilizer #13c: Examples of four-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of nitrogen (usually amine or imine groups) and are not contained in component heterocyclic rings (N-N Tridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: tetraazacyclooctane ([8]aneN₄); tetraazacyclononane ([9]aneN₄); tetraazacyclodecane ([10]aneN₄); tetraazacycloundecane ([11]aneN₄); tetraazacyclododecane ([12]aneN₄); tetraazacyclotridecane ([13]aneN₄); tetraazacyclotetradecane ([14]aneN₄); tetraazacyclopentadecane ([15]aneN₄); tetraazacyclohexadecane ([16]aneN₄); tetraazacycloheptadecane ([17]aneN₄); tetraazacyclooctadecane ([18]aneN₄); tetraazacyclononadecane ([19]aneN₄); tetraazacycloicosane ([20]aneN₄); tetraazacyclooctadiene ([8]dieneN₄); tetraazacyclononadiene ([9]dieneN₄); tetraazacyclodecadiene ([10]dieneN₄); tetraazacycloundecadiene ([11]dieneN₄); tetraazacyclododecadiene ([12]dieneN₄); tetraazacyclotridecadiene ([13]dieneN₄); tetraazacyclotetradecadiene ([14]dieneN₄); tetraazacyclopentadecadiene ([15]dieneN₄); tetraazacyclohexadecadiene ([16]dieneN₄); tetraazacycloheptadecadiene ([17]dieneN₄); tetraazacyclooctadecadiene ([18]dieneN₄); tetraazacyclononadecadiene ([19]dieneN₄); tetraazacycloicosadiene ([20]dieneN₄); tetraazacyclooctatetraene ([8]tetraeneN₄); tetraazacyclononetraene ([9]tetraeneN₄); tetraazacyclodecatetraene ([10]tetraeneN₄); tetraazacycloundecatetraene ([11]tetraeneN₄); tetraazacyclododecatetraene ([12]tetraeneN₄); tetraazacyclotridecatetraene ([13]tetraeneN₄); tetraazacyclotetradecatetraene ([14]tetraeneN₄); tetraazacyclopentadecatetraene ([15]tetraeneN₄); tetraazacyclohexadecatetraene ([16]tetraeneN₄); tetraazacycloheptadecatetraene ([17]tetraeneN₄); tetraazacyclooctadecatetraene ([18]tetraeneN₄); tetraazacyclononadecatetraene ([19]tetraeneN₄); and tetraazacycloicosatetraene ([20]tetraeneN₄).

N Valence Stabilizer #13d: Examples of six-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of nitrogen (usually amine or imine groups) and are not contained in component heterocyclic rings (N-N Tridentates, N-N Tetradentates, or N-N Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not

limited to: hexaazacyclododecane ([12]aneN₆); hexaazacyclotridecane ([13]aneN₆);
hexaazacyclotetradecane ([14]aneN₆); hexaazacyclopentadecane ([15]aneN₆);
hexaazacyclohexadecane ([16]aneN₆); hexaazacycloheptadecane ([17]aneN₆);
hexaazacyclooctadecane ([18]aneN₆); hexaazacyclononadecane ([19]aneN₆);
5 hexaazacycloicosane ([20]aneN₆); hexaazacycloheneicosane ([21]aneN₆);
hexaazacyclodocosane ([22]aneN₆); hexaazacyclotricosane ([23]aneN₆);
hexaazacyclotetracosane ([24]aneN₆); hexaazacyclododecatriene ([12]trieneN₆);
hexaazacyclotridecatriene ([13]trieneN₆); hexaazacyclotradecatriene ([14]trieneN₆);
hexaazacyclopentadecatriene ([15]trieneN₆); hexaazacyclohexadecatriene ([16]trieneN₆);
10 hexaazacycloheptadecatriene ([17]trieneN₆); hexaazacyclooctadecatriene ([18]trieneN₆);
hexaazacyclononadecatriene ([19]trieneN₆); hexaazacycloicosatriene ([20]trieneN₆);
hexaazacycloheneicosatriene ([21]trieneN₆); hexaazacyclodocosatriene ([22]trieneN₆);
hexaazacyclotricosatriene ([23]trieneN₆); and hexaazacyclotetracosatriene ([24]trieneN₆).

15 N Valence Stabilizer #13e: Examples of eight-membered macrocyclics, macrobicyclics, and
macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all
binding sites are composed of nitrogen (usually amine or imine groups) and are not contained in
component heterocyclic rings (N-N Tridentates, N-N Tetridentates, or N-N Hexadentates) that
meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not
20 limited to: octaazacyclohexadecane ([16]aneN₈); octaazacycloheptadecane ([17]aneN₈);
octaazacyclooctadecane ([18]aneN₈); octaazacyclononadecane ([19]aneN₈);
octaazacycloicosane ([20]aneN₈); octaazacycloheneicosane ([21]aneN₈); octaazacyclodocosane
([22]aneN₈); octaazacyclotricosane ([23]aneN₈); octaazacyclotetracosane ([24]aneN₈);
octaazacyclohexadecatetraene ([16]tetraeneN₈); octaazacycloheptadecatetraene
25 ([17]tetraeneN₈); octaazacyclooctadecatetraene ([18]tetraeneN₈);
octaazacyclononadecatetraene ([19]tetraeneN₈); octaazacycloicosatetraene
([20]tetraeneN₈); octaazacycloheneicosatetraene ([21]tetraeneN₈);
octaazacyclodocosatetraene ([22]tetraeneN₈); octaazacyclotricosatetraene
([23]tetraeneN₈); and octaazacyclotetracosatetraene ([24]tetraeneN₈).

N Valence Stabilizer #13f: Examples of ten-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of nitrogen (usually amine or imine groups) and are not contained in component heterocyclic rings (N-N Tridentates, N-N Tetridentates, or N-N Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: decaazacycloicosane ([20]aneN₁₀); decaazacycloheicosane ([21]aneN₁₀); decaazacyclodocosane ([22]aneN₁₀); decaazacyclotricosane ([23]aneN₁₀); decaazacyclotetacosane ([24]aneN₁₀); decaazacyclopentacosane ([25]aneN₁₀); decaazacyclohexacosane ([26]aneN₁₀); decaazacycloheptacosane ([27]aneN₁₀); decaazacyclooctacosane ([28]aneN₁₀); decaazacyclononacosane ([29]aneN₁₀); decaazacyclotricontane ([30]aneN₁₀); decaazacycloicosapentadiene ([20]pentadieneN₁₀); decaazacycloheneicosapentadiene ([21]pentadieneN₁₀); decaazacyclodocosapentadiene ([22]pentadieneN₁₀); decaazacyclotricosapentadiene ([23]pentadieneN₁₀); decaazacyclotracosapentadiene ([24]pentadieneN₁₀); decaazacyclopentacosapentadiene ([25]pentadieneN₁₀); decaazacyclohexacosapentadiene ([26]pentadieneN₁₀); decaazacycloheptacosapentadiene ([27]pentadieneN₁₀); decaazacyclooctacosapentadiene ([28]pentadieneN₁₀); decaazacyclononacosapentadiene ([29]pentadieneN₁₀); and decaazacyclotricontapentadiene ([30]pentadieneN₁₀).

N Valence Stabilizer #14a: Examples of four-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all four binding sites are composed of nitrogen and are contained in component 5-membered heterocyclic rings (N-N Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: porphyrins (including tetraphenylporphine (tpp); “picket fence” porphyrins, “picket tail” porphyrins, “bisocket” porphyrins, “capped” porphyrins, cyclophane porphyrins, “pagoda” porphyrins, “pocket” porphyrins, “pocket tail” porphyrins, cofacial diporphyrins, “strapped” porphyrins, “hanging base” porphyrins, bridged porphyrins, chelated mesoporphyrins, homoporphyrins, chlorophylls, and pheophytins); porphodimethanes; porphyrinogens; chlorins; bacteriochlorins; isobacteriochlorins; corroles; corrins and corrinoids; didehydrocorrins; tetradehydrocorrins; hexadehydrocorrins; octadehydrocorrins; tetraoxazoles; tetraisooxazoles; tetrathiazoles;

tetraisothiazoles; tetraazaphospholes; tetraimidazoles; tetrapyrrazoles; tetraoxadiazoles; tetrathiadiazoles; tetradiazaphospholes; tetratriazoles; tetraoxatriazoles; tetrathiatriazoles; coproporphyrin; etioporphyrin; and hematoporphyrin.

5 N Valence Stabilizer #14b: Examples of six-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all six binding sites are composed of nitrogen and are contained in component 5-membered heterocyclic rings (N-N Tridentates, N-N Tetridentates, or N-N Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to:
10 hexaphyrins (hexapyrroles); hexaoxazoles; hexaisooxazoles; hexathiazoles; hexaisothiazoles; hexaaazaphospholes; hexaimidazoles; hexapyrazoles; hexaoxadiazoles; hexathiadiazoles; hexadiazaphospholes; hexatriazoles; hexaoxatriazoles; and hexathiatriazoles.

15 N Valence Stabilizer #14c: Examples of eight-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all eight binding sites are composed of nitrogen and are contained in component 5-membered heterocyclic rings (N-N Tridentates, N-N Tetridentates, or N-N Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to:
20 octaphyrins (octapyrroles); octaoxazoles; octaisooxazoles; octathiazoles; octaisothiazoles; octaaazaphospholes; octaimidazoles; octapyrazoles; octaoxadiazoles; octathiadiazoles; octadiazaphospholes; octatriazoles; octaoxatriazoles; and octathiatriazoles.

25 N Valence Stabilizer #14d: Examples of ten-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all ten binding sites are composed of nitrogen and are contained in component 5-membered heterocyclic rings (N-N Tridentates, N-N Tetridentates, or N-N Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to:
30 decaphyrins (decapyrroles); decaoxazoles; decaisooxazoles; decathiazoles; decaisothiazoles; decaazaphospholes; decaimidazoles; decapyrazoles; decaoxadiazoles; decathiadiazoles; decadiazaphospholes; decatriazoles; decaoxatriazoles; and decathiatriazoles.

N Valence Stabilizer #15a: Examples of four-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all four binding sites are composed of nitrogen and are contained in a combination of 5-membered heterocyclic rings and amine or imine groups (N-N Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: porphyrazines; octahydrodiazaporphyrins; phthalocyanines; naphthalocyanines; anthracocyanines; and tetraazaporphyrins

N Valence Stabilizer #15b: Examples of six-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all six binding sites are composed of nitrogen and are contained in a combination of 5-membered heterocyclic rings and amine or imine groups (N-N Tridentates, N-N Tetridentates, or N-N Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diazahexaphyrins; tetraazahexaphyrins; hexaazahexaphyrins; diazahexapyrazoles; tetraazahexapyrazoles; hexaazahexapyrazoles; diazahexamidazoles; tetraazahexamidazoles; and hexaazahexamidazoles.

N Valence Stabilizer #15c: Examples of eight-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all eight binding sites are composed of nitrogen and are contained in a combination of 5-membered heterocyclic rings and amine or imine groups (N-N Tridentates, N-N Tetridentates, or N-N Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diazaoctaphyrins; tetraazaoctaphyrins; hexaazaoctaphyrins; octaazaoctaphyrins; diazoctapyrazoles; tetraazaoctapyrazoles; hexaazaoctapyrazoles; octaazaoctapyrazoles; diazoctaimidazoles; tetraazaoctaimidazoles; hexaazaoctaimidazoles; and octaazaoctaimidazoles.

N Valence Stabilizer #15d: Examples of ten-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all ten binding sites are composed of nitrogen and are contained in a combination of 5-membered heterocyclic rings and amine or imine groups (N-N Tridentates, N-N Tetridentates, or N-N

Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diazadecaphyrins; tetraazadecaphyrins; hexaaazadecaphyrins; octaaazadecaphyrins; decaazadecaphyrins; diazadecapryrazoles; tetraazadecapryrazoles; hexaaazadecapryrazoles; octaaazadecapryrazoles; decaazadecapryrazoles; diazadecaimidazoles; 5 tetraazadecaimidazoles; hexaaazadecaimidazoles; octaaazadecaimidazoles; and decaazadecaimidazoles.

N Valence Stabilizer #16a: Examples of four-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all 10 four binding sites are composed of nitrogen and are contained in component 6-membered heterocyclic rings (N-N Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: cyclotetrapyridines; cyclotetraoxazines; cyclotetrathiazines; cyclotetraphosphorins; cyclotetraquinolines; cyclotetrapryrazines; cyclotetrapyridazines; cyclotetrapirimidines; cyclotetraoxadiazines; 15 cyclotetrathiadiazines; cyclotetradiazaphosphorins; cyclotetraquinoxalines; cyclotetratriazines; cyclotetrathiatriazines; and cyclotetraoxatriazines.

N Valence Stabilizer #16b: Examples of six-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all 20 six binding sites are composed of nitrogen and are contained in component 6-membered heterocyclic rings (N-N Tridentates, N-N Tetridentates, or N-N Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: cyclosexipyridines; cyclosexioxazines; cyclosexithiazines; cyclosexiphosphorins; cyclosexiquinolines; cyclosexipyrazines; cyclosexipyridazines; cyclosexipyrimidines; 25 cyclosexioxadiazines; cyclosexithiadiazines; cyclosexidiazaphosphorins; cyclosexiquinoxalines; cyclosexitriazines; cyclosexithiatriazines; and cyclosexioxatriazines.

N Valence Stabilizer #16c: Examples of eight-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all 30 six binding sites are composed of nitrogen and are contained in component 6-membered heterocyclic rings (N-N Tridentates, N-N Tetridentates, or N-N Hexadentates) that meet the

requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to:
cyclooctapyridines; cyclooctaoxazines; cyclooctathiazines; cyclooctaphosphorins;
cyclooctaquinolines; cyclooctapyrazines; cyclooctapyridazines; cyclooctapyrimidines;
cyclooctaoxadiazines; cyclooctathiadiazines; cyclooctadiazaphosphorins; cyclooctaquinoxalines;
5 cyclooctatriazines; cyclooctathiatriazines; and cyclooctaoxatriazines.

N Valence Stabilizer #16d: Examples of ten-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all six binding sites are composed of nitrogen and are contained in component 6-membered
10 heterocyclic rings (N-N Tridentates, N-N Tetridentates, or N-N Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to:
cyclodecapyridines; cyclodecaoxazines; cyclodecathiazines; cyclodecaphosphorins;
cyclodecaquinolines; cyclodecapyrazines; cyclodecapyridazines; cyclodecapyrimidines;
cyclodecaoxadiazines; cyclodecathiadiazines; cyclodecadiazaphosphorins;
15 cyclodecaquinoxalines; cyclodecatriazines; cyclodecathiatriazines; and cyclodecaoxatriazines.

N Valence Stabilizer #17a: Examples of four-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all four binding sites are composed of nitrogen and are contained in a combination of 6-membered
20 heterocyclic rings and amine or imine groups (N-N Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to:
diazacyclotetrapyridines; tetraazacyclotetrapyridines; diazacyclotetraquinolines;
tetraazacyclotetraquinolines; diazacyclotetrapyrnazines; tetraazacyclotetrapyrnazines;
diazacyclotetrapyridazines; tetraazacyclotetrapyridazines; diazacyclotetrapyrimidines;
25 tetraazacyclotetrapyrimidines; diazacyclotetratriazines; and tetraazacyclotetratriazines.

N Valence Stabilizer #17b: Examples of six-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all six binding sites are composed of nitrogen and are contained in a combination of 6-membered
30 heterocyclic rings and amine or imine groups (N-N Tridentates, N-N Tetridentates, or N-N Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴

include, but are not limited to: diazacyclosexipyridines; triazacyclosexipyridines; diazacyclosexiquinolines; triazacyclosexiquinolines; diazacyclosexipyrazines; triazacyclosexipyrazines; diazacyclosexipyridazines; triazacyclosexipyridazines; diazacyclosexipyrimidines; triazacyclosexipyrimidines; diazacyclosexitriazines; and triazacyclosexitriazines.

5 N Valence Stabilizer #17c: Examples of eight-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all eight binding sites are composed of nitrogen and are contained in a combination of 6-membered 10 heterocyclic rings and amine or imine groups (N-N Tridentates, N-N Tetridentates, or N-N Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diazacyclooctapyridines; tetraazacyclooctapyridines; diazacyclooctaquinolines; tetraazacyclooctaquinolines; diazacyclooctapyrazines; tetraazacyclooctapyrazines; diazacyclooctapyridazines; tetraazacyclooctapyridazines; diazacyclooctapyrimidines; tetraazacyclooctapyrimidines; diazacyclooctatriazines; and tetraazacyclooctatriazines.

15 N Valence Stabilizer #17d: Examples of ten-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all ten binding sites are composed of nitrogen and are contained in a combination of 6-membered 20 heterocyclic rings and amine or imine groups (N-N Tridentates, N-N Tetridentates, or N-N Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diazacyclodecapyridines; pentaazacyclodecapyridines; diazacyclodecaquinolines; pentaazacyclodecaquinolines; diazacyclodecapyrazines; pentaazacyclodecapyrazines; diazacyclodecapyridazines; pentaazacyclodecapyridazines; diazacyclodecapyrimidines; pentaazacyclodecapyrimidines; diazacyclodecatriazines; and pentaazacyclodecatriazines.

25 N Valence Stabilizer #18: Examples of amidines and diamidines (N-N bidentates or N-N Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: N,N'-dimethylformamidine; N,N'-diethylformamidine; N,N'-

diisopropylformamidine; N,N'-dibutylformamidine; N,N'-diphenylformamidine; N,N'-dibenzylformamidine; N,N'-dinaphthylformamidine; N,N'-dicyclohexylformamidine; N,N'-dinorbornylformamidine; N,N'-diadamantylformamidine; N,N'-dianthraquinonylformamidine; N,N'-dimethylacetamide; N,N'-diethylacetamide; N,N'-diisopropylacetamide; N,N'-dibutylacetamide; N,N'-diphenylacetamide; N,N'-dibenzylacetamide; N,N'-dinaphthylacetamide; N,N'-dicyclohexylacetamide; N,N'-dinorbornylacetamide; N,N'-diadamantylacetamide; N,N'-dimethylbenzamide; N,N'-diethylbenzamide; N,N'-diisopropylbenzamide; N,N'-dibutylbenzamide; N,N'-diphenylbenzamide; N,N'-dibenzylbenzamide; N,N'-dinaphthylbenzamide; N,N'-dicyclohexylbenzamide; N,N'-dinorbornylbenzamide; N,N'-diadamantylbenzamide; N,N'-dimethyltoluamide; N,N'-diethyltoluamide; N,N'-diisopropyltoluamide; N,N'-dibutyltoluamide; N,N'-diphenyltoluamide; N,N'-dibenzyltoluamide; N,N'-dinaphthyltoluamide; N,N'-dicyclohexyltoluamide; N,N'-dinorbornyltoluamide; N,N'-diadamantyltoluamide; oxalic diamidine; malonic diamidine; succinic diamidine; glutaric diamidine; adipic diamidine; pimelic diamidine; suberic diamidine; phthalic diamidine; terephthalic diamidine; isophthalic diamidine; piperazine diamidine; 2-iminopyrrolidine; 2-iminopiperidine; amidinobenzamide; benzamide; chloroazodin; and debrisoquin.

N Valence Stabilizer #19: Examples of biguanides (imidodicarbonimidic diamides), biguanidines, imidotricarbonimidic diamides, imidotetracarbonimidic diamides, dibiguanides, bis(biguanidines), polybiguanides, and poly(biguanidines) (N-N bidentates, N-N tridentates, N-N tetridentates, and N-N hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: biguanide (bigH); biguanidine, methylbiguanide; ethylbiguanide; isopropylbiguanide; butylbiguanide; benzylbiguanide; phenylbiguanide; tolylbiguanide; naphthylbiguanide; cyclohexylbiguanide; norbornylbiguanide; adamantlylbiguanide; dimethylbiguanide; diethylbiguanide; diisopropylbiguanide; dibutylbiguanide; dibenzylbiguanide; diphenylbiguanide; ditolylbiguanide; dinaphthylbiguanide; dicyclohexylbiguanide; dinorbornylbiguanide; diadamantylbiguanide; ethylenedibiguanide; propylenedibiguanide; tetramethylenedibiguanide; pentamethylenedibiguanide; hexamethylenedibiguanide; heptamethylenedibiguanide; octamethylenedibiguanide; phenylenedibiguanide; piperazinedibiguanide; oxalyldibiguanide; malonyldibiguanide;

succinylbibiguanide; glutarylribiguanide; adipyribiguanide; pimelyribiguanide; suberyribiguanide; phthalyribiguanide; paludrine; polyhexamethylene biguanide; 2-guanidinothiazole; 2-guanidinooxazole; 2-guanidinoimidazole; 3-guanidinopyrazole; 3-guanidino-1,2,4-triazole; 5-guanidinotetrazole; alexidine; buformin; and moroxydine.

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N Valence Stabilizer #20: Examples of diamidinomethanes, bis(diamidinomethanes), and poly(diamidinomethanes) (N-N bidentates, N-N tridentates, N-N tetridentates, and N-N hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diamidinomethane; N-methyldiamidinomethane; N-ethylidiamidinomethane; N-isopropylidiamidinomethane; N-butyldiamidinomethane; N-benzylidiamidinomethane; N-phenyldiamidinomethane; N-tolyldiamidinomethane; N-naphthyldiamidinomethane; N-cyclohexyldiamidinomethane; N-norbornyldiamidinomethane; N-adamantyldiamidinomethane; dimethyldiamidinomethane; diethyldiamidinomethane; diisopropylidiamidinomethane; dibutylidiamidinomethane; dibenzylidiamidinomethane; diphenylidiamidinomethane; ditolyldiamidinomethane; dinaphthyldiamidinomethane; dicyclohexyldiamidinomethane; dinorbornyldiamidinomethane; diadamantyldiamidinomethane; ethylenebisdiamidinomethane; propylenebisdiamidinomethane; tetramethylenebisdiamidinomethane; pentamethylenebisdiamidinomethane; hexamethylenebisdiamidinomethane; heptamethylenebisdiamidinomethane; octamethylenebisdiamidinomethane; phenylenebisdiamidinomethane; piperazinebisdiamidinomethane; oxalylbisdiamidinomethane; malonylbisdiamidinomethane; succinylbisdiamidinomethane; glutarylbisdiamidinomethane; phthalylbisdiamidinomethane; 2-amidinomethylthiazole; 2-amidinomethyloxazole; 2-amidinomethylimidazole; 3-amidinomethylpyrazole; 3-amidinomethyl-1,2,4-triazole; and 5-amidinomethyltetrazole.

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N Valence Stabilizer #21: Examples of imidoylguanidines, amidinoguanidines, bis(imidoylguanidines), bis(amidinoguanidines), poly(imidoylguanidines), and poly(amidinoguanidines) (N-N bidentates, N-N tridentates, N-N tetridentates, and N-N hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: acetimidoylguanidine; amidinoguanidine, benzimidoylguanidine; cyclohexylimidoylguanidine; pentafluorobenzimidoylguanidine; 2-N-imidoylaminothiazole; 2-

N-imidoylaminooxazole; 2-N-imidoylaminoimidazole; 3-N-imidoylaminopyrazole; 3-N-imidoylamino-1,2,4-triazole; and 5-N-imidoylaminotetrazole.

N Valence Stabilizer #22: Examples of diformamidine oxides (dicarbonimidic diamides), tricarbonimidic diamides, tetracarbonimidic diamides, bis(difomamidine oxides), and poly(difomamidine oxides) (N-N bidentates, N-N tridentates, or N-N tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diformamidine oxide; methyldifomamidine oxide; ethyldifomamidine oxide; isopropyldifomamidine oxide; butyldifomamidine oxide; benzylidifomamidine oxide; phenyldifomamidine oxide; tolyldifomamidine oxide; naphthyldifomamidine oxide; cyclohexyldifomamidine oxide; norbornyldifomamidine oxide; adamantlyldifomamidine oxide; dimethyldifomamidine oxide; diethyldifomamidine oxide; diisopropyldifomamidine oxide; dibutyldifomamidine oxide; dibenzylidifomamidine oxide; diphenyldifomamidine oxide; ditolyldifomamidine oxide; dinaphthyldifomamidine oxide; dicyclohexyldifomamidine oxide; dinorbornyldifomamidine oxide; diadamantlyldifomamidine oxide; 2-O-amidinohydroxythiazole; 2-O-amidinohydroxyoxazole; 2-O-amidinohydroxyimidazole; 3-O-amidinohydroxypyrazole; 3-O-amidinohydroxy-1,2,4-triazole; and 5-O-amidinohydroxytetrazole.

N Valence Stabilizer #23: Examples of diformamidine sulfides (thiodicarbonimidic diamides), thiotricarbonimidic diamides, thiotetracarbonimidic diamides, bis(difomamidine sulfides), and poly(difomamidine sulfides) (N-N bidentates, N-N tridentates, or N-N tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diformamidine sulfide; methyldifomamidine sulfide; ethyldifomamidine sulfide; isopropyldifomamidine sulfide; butyldifomamidine sulfide; benzylidifomamidine sulfide; phenyldifomamidine sulfide; tolyldifomamidine sulfide; naphthyldifomamidine sulfide; cyclohexyldifomamidine sulfide; norbornyldifomamidine sulfide; adamantlyldifomamidine sulfide; dimethyldifomamidine sulfide; diethyldifomamidine sulfide; diisopropyldifomamidine sulfide; dibutyldifomamidine sulfide; dibenzylidifomamidine sulfide; diphenyldifomamidine sulfide; ditolyldifomamidine sulfide; dinaphthyldifomamidine sulfide;

dicyclohexyldiformamidine sulfide; dinorbornyldiformamidine sulfide;
diadamantyldiformamidine sulfide; phenylthiobisformamidine;
2-S-amidinomercaptothiazole; 2-S-amidinomercaptooxazole; 2-S-amidinomercaptoimidazole; 3-
S-amidinomercaptopyrazole; 3-S-amidinomercapto-1,2,4-triazole; and 5-S-
5 amidinomercaptotetrazole.

N Valence Stabilizer #24: Examples of imidodicarbonimidic acids, diimidodicarbonimidic acids,
imidotricarbonimidic acids, imidotetracarbonimidic acids, and derivatives thereof (N-N
Bidentates, N-N Tridentates, N-N Tetridentates, and N-N Hexadentates) that meet the
10 requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to:
imidodicarbonimidic acid, diimidodicarbonimidic acid, imidotricarbonimidic acid,
imidotetracarbonimidic acid; O-methylimidodicarbonimidic acid; O-ethylimidodicarbonimidic
acid; O-isopropylimidodicarbonimidic acid; O-phenylimidodicarbonimidic acid; O-
benzylimidodicarbonimidic acid; O-cyclohexylimidodicarbonimidic acid; O-
15 naphthylimidodicarbonimidic acid; O-norbornylimidodicarbonimidic acid; O-
adamantylimidodicarbonimidic acid; O,O'-dimethylimidodicarbonimidic acid; O,O'-
diethylimidodicarbonimidic acid; O,O'-diisopropylimidodicarbonimidic acid; O,O'-
diphenylimidodicarbonimidic acid; O,O'-dibenzylimidodicarbonimidic acid; O,O'-
20 dicyclohexylimidodicarbonimidic acid; O,O'-dinaphthylimidodicarbonimidic acid; O,O'-
dinorbornylimidodicarbonimidic acid; and O,O'-diadamantylimidodicarbonimidic acid.

N Valence Stabilizer #25: Examples of thioimidodicarbonimidic acids,
thiodiimidodicarbonimidic acids, thioimidotricarbonimidic acids, thioimidotetracarbonimidic
acids, and derivatives thereof (N-N Bidentates, N-N Tridentates, N-N Tetridentates, and N-N
25 Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴
include, but are not limited to: thioimidodicarbonimidic acid, thiodiimidodicarbonimidic acid,
thioimidotricarbonimidic acid, thioimidotetracarbonimidic acid; O-
methylthioimidodicarbonimidic acid; O-ethylthioimidodicarbonimidic acid; O-
30 isopropylthioimidodicarbonimidic acid; O-phenylthioimidodicarbonimidic acid; O-
benzylthioimidodicarbonimidic acid; O-cyclohexylthioimidodicarbonimidic acid; O-
naphthylthioimidodicarbonimidic acid; O-norbornylthioimidodicarbonimidic acid; O-

adamantylthioimidodicarbonimidic acid; O,O'-dimethylthioimidodicarbonimidic acid; O,O'-diethylthioimidodicarbonimidic acid; O,O'-diisopropylthioimidodicarbonimidic acid; O,O'-diphenylthioimidodicarbonimidic acid; O,O'-dibenzylthioimidodicarbonimidic acid; O,O'-dicyclohexylthioimidodicarbonimidic acid; O,O'-dinaphthylthioimidodicarbonimidic acid; O,O'-
5 dinorbornylthioimidodicarbonimidic acid; and O,O'-diadamantylthioimidodicarbonimidic acid.

N Valence Stabilizer #26: Examples of diimidoylimines, diimidoylhydrazides, bis(diimidoylimines), bis(diimidoylhydrazides), poly(diimidoylimines), and poly(diimidoylhydrazides) (N-N Tridentates and N-N Hexadentates) that meet the requirements
10 for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to:
diacetimidoylimine; dibenzimidoylimine; and dicyclohexylimidoylimine.

N Valence Stabilizer #27: Examples of imidosulfamides, diimidosulfamides, bis(imidosulfamides), bis(diimidosulfamides), poly(imidosulfamides), and poly(diimidosulfamides) (N-N Bidentates, N-N Tridentates, N-N Tetridentates, and N-N Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴
15 include, but are not limited to: imidosulfamic acid, diimidosulfamic acid; O-phenylimidosulfamide; O-benzylimidosulfamide; N-phenylimidosulfamide; N-benzylimidosulfamide; O-phenyldiimidosulfamide; O-benzyldiimidosulfamide; N-phenyldiimidosulfamide; and N-benzyldiimidosulfamide.
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N Valence Stabilizer #28: Examples of phosphoramidimidic triamides, bis(phosphoramidimidic triamides), and poly(phosphoramidimidic triamides) and derivatives thereof (N-N Bidentates, N-N Tridentates, N-N Tetridentates, and N-N Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: phosphoramidimidic triamide; N-phenylphosphoramidimidic triamide; N-benzylphosphoramidimidic triamide; N-naphthylphosphoramidimidic triamide; N-cyclohexylphosphoramidimidic triamide; N-norbornylphosphoramidimidic triamide; N,N'-diphenylphosphoramidimidic triamide; N,N'-dibenzylphosphoramidimidic triamide; N,N'-dinaphthylphosphoramidimidic triamide; N,N'-dicyclohexylphosphoramidimidic triamide; and N,N'-dinorbornylphosphoramidimidic triamide.
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N Valence Stabilizer #29: Examples of phosphoramidimidic acid, phosphorodiamidimidic acid, bis(phosphoramidimidic acid), bis(phosphorodiamidimidic acid), poly(phosphoramidimidic acid), poly(phosphorodiamidimidic acid), and derivatives thereof (N-N Bidentates, N-N Tridentates, N-N Tetridentates, and N-N Hexadentates) that meet the requirements for use as
5 “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: phosphoramidimidic acid, phosphorodiamidimidic acid, O-phenylphosphoramidimidic acid; O-benzylphosphoramidimidic acid; O-naphthylphosphoramidimidic acid; O-cyclohexylphosphoramidimidic acid; O-norbornylphosphoramidimidic acid; O,O'-diphenylphosphoramidimidic acid; O,O'-dibenzylphosphoramidimidic acid; O,O'-dinaphthylphosphoramidimidic acid; O,O'-dicyclohexylphosphoramidimidic acid; and O,O'-dinorbornylphosphoramidimidic acid.

N Valence Stabilizer #30: Examples of phosphoramidimidodithioic acid, phosphorodiamidimidodithioic acid, bis(phosphoramidimidodithioic acid), bis(phosphorodiamidimidodithioic acid), poly(phosphoramidimidodithioic acid), poly(phosphorodiamidimidodithioic acid), and derivatives thereof (N-N Bidentates, N-N Tridentates, N-N Tetridentates, and N-N Hexadentates) that meet the requirements for use as
15 “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to:
phosphoramidimidodithioic acid, phosphorodiamidimidodithioic acid, S-phenylphosphoramidimidodithioic acid; S-benzylphosphoramidimidodithioic acid; S-naphthylphosphoramidimidodithioic acid; S-cyclohexylphosphoramidimidodithioic acid; S-norbornylphosphoramidimidodithioic acid; S,S'-diphenylphosphoramidimidodithioic acid; S,S'-dibenzylphosphoramidimidodithioic acid; S,S'-dinaphthylphosphoramidimidodithioic acid; S,S'-dicyclohexylphosphoramidimidodithioic acid; and S,S'-dinorbornylphosphoramidimidodithioic acid.

N Valence Stabilizer #31: Examples of azo compounds with amino, imino, oximo, diazeno, or hydrazido substitution at the ortho- (for aryl) or alpha- or beta- (for alkyl) positions, bis[o-(H₂N-)] or alpha- or beta-(H₂N-)azo compounds], or poly[o-(H₂N-) or alpha- or beta-(H₂N-)azo compounds] (N-N Bidentates, N-N Tridentates, N-N Tetridentates, or N-N Hexadentates) that
30 meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not

limited to: o-aminoazobenzene; o,o'-diaminoazobenzene; (2-pyridine)azobenzene; 1-phenylazo-2-naphthylamine; pyridineazo-2-naphthol (PAN); pyridineazoresorcinol (PAR); o-hydroxy-o'-(beta-aminoethylamino)azobenzene; Benzopurpurin 4B; Congo Red; Fat Brown RR; 5 benzopurpurin; Congo Red; Direct Red 75; Mordant Brown 48; Nitro Red; 2-imidazolylazobenzene; 2-benzimidazolylazobenzene; 3-pyrazolylazobenzene; 3-(1,2,4-triazolyl)azobenzene; 2-pyridylazobenzene; 2-pyrazinylazobenzene; and 2-pyrimidinylazobenzene.

10 N Valence Stabilizer #32: Examples of diazeneformimidamides (diazeneamidines), diazeneacetimidamides (diazene-alpha-amidinoalkanes(alkenes)), bis(diazeneformimidamides), bis(diazeneacetimidamides), poly(diazeneformimidamides), and poly(diazeneacetimidamides) (N-N Bidentates, N-N Tetridentates, and N-N Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to:
15 diazeneformimidamide (diazeneamidine); diazeneacetimidamide (diazene-alpha-amidinomethane); phenyldiazeneformimidamide; triphenyldiazeneformimidamide; phenyldiazeneacetimidamide; and triphenyldiazeneacetimidamide.

20 N Valence Stabilizer #33: Examples of diazeneformimidic acid, diazeneacetimidic acid, bis(diazeneformimidic acid), bis(diazeneacetimidic acid), poly(diazeneformimidic acid), poly(diazeneacetimidic acid), and derivatives thereof (N-N Bidentates, N-N Tetridentates, and N-N Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diazeneformimidic acid, diazeneacetimidic acid, phenyldiazeneformimidic acid, diphenyldiazeneformimidic acid, phenyldiazeneacetimidic acid, and diphenyldiazeneacetimidic acid.

25 N Valence Stabilizer #34: Examples of diazeneformimidothioic acid, diazeneacetimidothioic acid, bis(diazeneformimidothioic acid), bis(diazeneacetimidothioic acid), poly(diazeneformimidothioic acid), poly(diazeneacetimidothioic acid), and derivatives thereof (N-N Bidentates, N-N Tetridentates, and N-N Hexadentates) that meet the requirements for use 30 as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to:
diazeneformimidothioic acid, diazeneacetimidothioic acid, phenyldiazeneformimidothioic acid,

diphenyldiazeneformimidothioic acid, phenyldiazeneacetimidothioic acid, and diphenyldiazeneacetimidothioic acid.

N Valence Stabilizer #35: Examples of imidoyleldiazenes, bis(imidoyleldiazenes), and

5 poly(imidoyleldiazenes), (N-N Tridentates and N-N Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: acetimidoyldiazene; benzimidoyldiazene; and cyclohexylimidoyldiazene.

N Valence Stabilizer #36: Examples of diazenediformimidamides (1,2-diazenediamidines),

10 diazenediacetimidamides (1,2-diazene-di-alpha-amidinoalkanes(alkenes)), bis(diazenediformimidamides), bis(diazenediacetimidamides), poly(diazenediformimidamides), and poly(diazenediacetimidamides) (N-N Tridentates and N-N Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diazenediformimidamide (1,2-diazenediamidine), diazenediacetimidamide (1,2-diazene-di-alpha-amidinomethane); diphenyldiazenediformimidamide; tetraphenyldiazenediformimidamide; diphenyldiazenediacetimidamide; and tetraphenyldiazenediacetimidamide.

N Valence Stabilizer #37: Examples of diazenediformimidic acid, diazenediacetimidic acid,

20 bis(diazenediformimidic acid), bis(diazenediacetimidic acid), poly(diazenediformimidic acid), and poly(diazenediacetimidic acid), and derivatives thereof (N-N Tridentates and N-N Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diazenediformimidic acid, diazenediacetimidic acid, diphenyldiazenediformimidic acid, and diphenyldiazenediacetimidic acid.

25 N Valence Stabilizer #38: Examples of diazenediformimidothioic acid, diazenediacetimidothioic

acid, bis(diazenediformimidothioic acid), bis(diazenediacetimidothioic acid), poly(diazenediformimidothioic acid), and poly(diazenediacetimidothioic acid), and derivatives thereof (N-N Tridentates and N-N Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diazenediformimidothioic acid, diazenediacetimidothioic acid, diphenyldiazenediformimidothioic acid, and diphenyldiazenediacetimidothioic acid.

N Valence Stabilizer #39: Examples of diimidoyldiazenes, bis(diimidoyldiazenes), and poly(diimidoyldiazenes), (N-N Tridentates and N-N Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diacetimidoyldiazene; dibenzimidoyldiazene; and dicyclohexylimidoyldiazene.

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N Valence Stabilizer #40: Examples of ortho-amino (or -hydrazido) substituted formazans, bis(o-amino or -hydrazido substituted formazans), and poly(o-amino or -hydrazido substituted formazans) (N-N Bidentates, N-N Tridentates, N-N Tetridentates, and N-N Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 1-(2-aminophenyl)-3,5-diphenylformazan; and 1,5-bis(2-aminophenyl)-3-phenylformazan.

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N Valence Stabilizer #41: Examples of ortho-amino (or -hydrazido) substituted azines (including ketazines), bis(o-amino or hydrazido substituted azines), and poly(o-amino or hydrazido substituted azines) (N-N Bidentates, N-N Tridentates, N-N Tetridentates, and N-N Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-amino-1-benzalazine; 2-amino-1-naphthalazine; and 2-amino-1-cyclohexanonazine.

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N Valence Stabilizer #42: Examples of Schiff Bases with one Imine (C=N) Group and with ortho- or alpha- or beta-amino or imino or oximo or diazeno or hydrazido substitution (N-N Bidentates, N-N Tridentates, N-N Tetridentates, N-N Pentadentates, or N-N Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: N-(2-Aminobenzaldehydo)isopropylamine; N-(2-

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Pyridinecarboxaldehydo)isopropylamine; N-(2-Pyrrolecarboxaldehydo)isopropylamine; N-(2-Acetylpyridino)isopropylamine; N-(2-Acetylpyrrolo)isopropylamine; N-(2-Aminoacetophenono)isopropylamine; N-(2-Aminobenzaldehydo)cyclohexylamine; N-(2-Pyridinecarboxaldehydo)cyclohexylamine; N-(2-Pyrrolecarboxaldehydo)cyclohexylamine; N-(2-Acetylpyridino)cyclohexylamine; N-(2-Acetylpyrrolo)cyclohexylamine; N-(2-Aminoacetophenono)cyclohexylamine; N-(2-Aminobenzaldehydo)aniline; N-(2-Pyridinecarboxaldehydo)aniline; N-(2-Pyrrolecarboxaldehydo)aniline; N-(2-

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Acetylpyridino)aniline; N-(2-Acetylpyrrolo)aniline; N-(2-Aminoacetophenono)aniline; N-(2-Aminobenzaldehydo)aminonorbornane; N-(2-Pyridinecarboxaldehydo)aminonorbornane; N-(2-Pyrrolecarboxaldehydo)aminonorbornane; N-(2-Acetylpyridino)aminonorbornane; N-(2-Acetylpyrrolo)aminonorbornane; N-(2-Aminoacetophenono)aminonorbornane; 2-pyrrolecarboxaldehyde phenylhydrazone; 2-pyrrolecarboxaldehyde 2-pyridyl hydrazone; 2-aminobenzaldehyde phenylhydrazone (nitrin); and 2-aminobenzaldehyde 2-pyridyl hydrazone.
Also includes hydrazones with ortho-N substitution.

5 N Valence Stabilizer #43: Examples of Schiff Bases with two Imine (C=N) Groups and without
10 ortho- (for aryl constituents) or alpha- or beta- (for alkyl constituents) hydroxy, carboxy,
 carbonyl, thiol, mercapto, thiocarbonyl, amino, imino, oximo, diazeno, or hydrazido substitution
 (N-N Bidentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴
 include, but are not limited to: N,N’-(Glyoxalo)diisopropylamine; N,N’-(Glyoxalo)dicyclohexylamine;
15 N,N’-(Malondialdehydo)diisopropylamine; N,N’-(Malondialdehydo)dicyclohexylamine; N,N’-(Malondialdehydo)dianiline; N,N’-(Malondialdehydo)di-aminonorbornane; N,N’-(Phthalicdialdehydo)diisopropylamine; N,N’-(Phthalicdialdehydo)dicyclohexylamine; N,N’-(Phthalicdialdehydo)dianiline; N,N’-(Phthalicdialdehydo)di-aminonorbornane; N,N’-(Formylcamphoro)diisopropylamine; N,N’-(Formylcamphoro)dicyclohexylamine; N,N’-(Formylcamphoro)dianiline; N,N’-(Formylcamphoro)di-aminonorbornane; N,N’-(Acetylacetonato)diisopropylamine; N,N’-(Acetylacetonato)dicyclohexylamine; N,N’-(Acetylacetonato)dianiline; N,N’-(Acetylacetonato)di-aminonorbornane; N,N’-(Diacetylbenzeno)diisopropylamine; N,N’-(Diacetylbenzeno)dicyclohexylamine; N,N’-(Diacetylbenzeno)dianiline; N,N’-(Diacetylbenzeno)di-aminonorbornane; N,N’-(1,2-Cyclohexanono)diisopropylamine; N,N’-(1,2-Cyclohexanono)dicyclohexylamine; N,N’-(1,2-Cyclohexanono)dianiline; N,N’-(1,2-Cyclohexanono)di-aminonorbornane; N,N’-(Camphorquinono)diisopropylamine; N,N’-(Camphorquinono)dicyclohexylamine; N,N’-(Camphorquinono)dianiline; N,N’-(Camphorquinono)di-aminonorbornane; N,N’-(Benzaldehydo)ethylenediamine; N,N’-(Naphthaldehydo)ethylenediamine; N,N’-(Acetophenono)ethylenediamine; N,N’-(Benzaldehydo)trimethylenediamine; N,N’-(Naphthaldehydo)trimethylenediamine; N,N’-(Acetophenono)trimethylenediamine; ; N,N’-

(Benzaldehydo)cyclohexane-1,2-diamine; N,N'-(Naphthaldehydo)cyclohexane-1,2-diamine; N,N'-(Acetophenono)cyclohexane-1,2-diamine; N,N'-(Benzaldehydo)-1,2-diaminobenzene; N,N'-(Naphthaldehydo)-1,2-diaminobenzene; N,N'-(Acetophenono)-1,2-diaminobenzene; N,N'-(Acetylacetato)ethylenediamine; N,N'-(Acetylacetato)-1,2-cyclohexylenediamine; N,N'-(Acetylacetato)-1,2-propylenediamine; N,N'-(Glyoxalo)-o-phenylenediamine; and N,N'-(Glyoxalo)ethylenediamine. Also includes dihydrazones.

N Valence Stabilizer #44: Examples of Schiff Bases with two Imine (C=N) Groups and with
ortho- or alpha- or beta-amino or imino or oximo or diazeno or hydrazido substitution (N-N
10 Bidentates, N-N Tridentates, N-N Tetridentates, N-N Pentadentates, or N-N Hexadentates) that
meet the requirements for use as "wide band" valence stabilizers for Ce⁺⁴ include, but are not
limited to: N,N'-(2,6-Pyridinedicarboxaldehydo)diisopropylamine; N,N'-(2,6-
Pyridinedicarboxaldehydo)dicyclohexylamine; N,N'-(2,6-Pyridinedicarboxaldehydo)dianiline;
N,N'-(2,6-Pyridinedicarboxaldehydo)di-aminonorbornane; N,N'-(2,5-
15 Pyrroledicarboxaldehydo)diisopropylamine; N,N'-(2,5-
Pyrroledicarboxaldehydo)dicyclohexylamine; N,N'-(2,5-Pyrroledicarboxaldehydo)dianiline;
N,N'-(2,5-Pyrroledicarboxaldehydo)di-aminonorbornane; N,N'-(o-
Aminophthalicdialdehydo)diisopropylamine; N,N'-(o-
Aminophthalicdialdehydo)dicyclohexylamine; N,N'-(o-Aminophthalicdialdehydo)dianiline;
20 N,N'-(o-Aminophthalicdialdehydo)di-aminonorbornane; N,N'-(o-
Aminoformylcamphoro)diisopropylamine; N,N'-(o-Aminoformylcamphoro)dicyclohexylamine;
N,N'-(o-Aminoformylcamphoro)dianiline; N,N'-(o-Aminoformylcamphoro)di-
aminonorbornane; N,N'-(2,6-Diacetylpyridino)diisopropylamine; N,N'-(2,6-
Diacetylpyridino)dicyclohexylamine; N,N'-(2,6-Diacetylpyridino)dianiline; N,N'-(2,6-
25 Diacetylpyridino)di-aminonorbornane; N,N'-(o-Aminodiacylbenzeno)diisopropylamine; N,N'-(
(o-Aminodiacylbenzeno)dicyclohexylamine; N,N'-(o-Aminodiacylbenzeno)dianiline; N,N'-(
(o-Aminodiacylbenzeno)di-aminonorbornane; N,N'-(3,6-Diamino-1,2-
cyclohexanono)diisopropylamine; N,N'-(3,6-Diamino-1,2-cyclohexanono)dicyclohexylamine;
N,N'-(3,6-Diamino-1,2-cyclohexanono)dianiline; N,N'-(3,6-Diamino-1,2-cyclohexanono)di-
30 aminonorbornane; N,N'-(2,5-Diacetylpyrrolo)diisopropylamine; N,N'-(2,5-
Diacetylpyrrolo)dicyclohexylamine; N,N'-(2,5-Diacetylpyrrolo)dianiline; N,N'-(2,5-

Diacetylpyrrolo)di-aminonorbornane; N,N'-(o-Aminobenzaldehydo)ethylenediamine; N,N'-(o-Aminonaphthaldehydo)ethylenediamine; N,N'-(o-Aminoacetophenono)ethylenediamine; ; N,N'-(o-Aminobenzaldehydo)trimethylenediamine; N,N'-(o-Aminonaphthaldehydo)trimethylenediamine; N,N'-(o-Aminoacetophenono)trimethylenediamine; ; N,N'-(o-Aminobenzaldehydo)cyclohexane-1,2-diamine; N,N'-(o-Aminonaphthaldehydo)cyclohexane-1,2-diamine; N,N'-(o-Aminoacetophenono)cyclohexane-1,2-diamine; N,N'-(o-Aminobenzaldehydo)-1,2-diaminobenzene; N,N'-(o-Aminonaphthaldehydo)-1,2-diaminobenzene; and N,N'-(o-Aminoacetophenono)-1,2-diaminobenzene. Also includes hydrazones with ortho-N substitution.

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N Valence Stabilizer #45: Examples of Schiff Bases with three Imine (C=N) Groups and without ortho- (for aryl constituents) or alpha- or beta- (for alkyl constituents) hydroxy, carboxy, carbonyl, thiol, mercapto, thiocarbonyl, amino, imino, oximo, diazeno, or hydrazido substitution (N-N Tridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: N,N',N''-(Benzaldehydo)tris(2-aminoethyl)amine; N,N',N''-(Naphthaldehydo)tris(2-aminoethyl)amine; and N,N',N''-(Acetophenono)tris(2-aminoethyl)amine. Also includes trihydrazones.

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N Valence Stabilizer #46: Examples of Schiff Bases with three Imine (C=N) Groups and with ortho- or alpha- or beta-amino or imino or oximo or diazeno or hydrazido substitution (N-N Tridentates, N-N Tetridentates, N-N Pentadentates, or N-N Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: N,N',N''-(o-Aminobenzaldehydo)tris(2-aminoethyl)amine; N,N',N''-(o-Aminonaphthaldehydo)tris(2-aminoethyl)amine; and N,N',N''-(o-Aminoacetophenono)tris(2-aminoethyl)amine.

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S Valence Stabilizer #1: Examples of macrocyclic, macrobicyclic, and macropolycyclic oligothioketones (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of thioketones (especially in the beta position) (S-S Bidentates, S-S Tetridentates, and S-S Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: hexathioketocyclotetracosane ([24]ane(=S)₆);

hexathioketocyclohexeneicosane ([21]ane(=S)₆); hexathioketocyclooctadecane ([18]ane(=S)₆);
hexathioketocyclopentadecane ([15]ane(=S)₆); tetrathioketocyclohexeicosane ([20]ane(=S)₄);
tetrathioketocyclooctadecane ([18]ane(=S)₄); tetrathioketocyclohexadecane ([16]ane(=S)₄);
tetrathioketocyclotetradecane ([14]ane(=S)₄); tetrathioketocyclododecane ([12]ane(=S)₄);
5 dithioketocyclohexadecane ([16]ane(=S)₂); dithioketocyclotetraadecane ([14]ane(=S)₂);
dithioketocyclododecane ([12]ane(=S)₂); dithioketocyclodecane ([10]ane(=S)₂); and
dithioketocyclooctane ([8]ane(=S)₂).

S Valence Stabilizer #2: Examples of macrocyclic, macrobicyclic, and macropolycyclic
10 dithiolenes (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding
sites are composed of alpha-, alpha-dithiolenes (meaning two thiol groups on a single carbon
atom in the ring) (S-S Bidentates, S-S Tetridentates, and S-S Hexadentates) that meet the
requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to:
hexathiolocyclotetracosane ([24]ane(-SH)₆); hexathiolocyclohexeneicosane ([21]ane(-SH)₆);
15 hexathiolocyclooctadecane ([18]ane(-SH)₆); hexathiolocyclopentadecane ([15]ane(-SH)₆);
tetrathiolocyclohexeicosane ([20]ane(-SH)₄); tetrathiolocyclooctadecane ([18]ane(-SH)₄);
tetrathiolocyclohexadecane ([16]ane(-SH)₄); tetrathiolocyclotetradecane ([14]ane(-SH)₄);
tetrathiolocyclododecane ([12]ane(-SH)₄); dithiolocyclohexadecane ([16]ane(-SH)₂);
dithiolocyclotetraadecane ([14]ane(-SH)₂); dithiolocyclododecane ([12]ane(-SH)₂);
20 dithiolocyclodecane ([10]ane(-SH)₂); and dithiolocyclooctane ([8]ane(-SH)₂).

S Valence Stabilizer #3: Examples of dithioimidodialdehydes, dithiohydrazidodialdehydes
(thioacyl thiohydrazides), bis(dithioimidodialdehydes), bis(dithiohydrazidodialdehydes),
poly(dithioimidodialdehydes), and poly(dithiohydrazidodialdehydes) (S-S Bidentates, S-S
25 Tridentates, S-S Tetridentates) that meet the requirements for use as “wide band” valence
stabilizers for Ce⁺⁴ include, but are not limited to: dithiodiacetamide, dithiodipropanamide,
dithiodibutanamide, dithiodibenzamide, and dithiodicyclohexamide.

S Valence Stabilizer #4: Examples of dithioimidodicarbonic acids, dithiohydrazidodicarbonic
30 acids, bis(dithioimidodicarbonic acids), bis(dithiohydrazidodicarbonic acids),
poly(dithioimidodicarbonic acids), poly(dithiohydrazidodicarbonic acids) and derivatives thereof

(S-S Bidentates, S-S Tridentates, S-S Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dithioimidodicarbonic acid, dithiohydrazidodicarbonic acid, O-phenyldithioimidodicarbonic acid, O-benzylidithioimidodicarbonic acid, O-cyclohexyldithioimidodicarbonic acid, O-norbornyldithioimidodicarbonic acid, O,O'-diphenyldithioimidodicarbonic acid, O,O'-dibenzylidithioimidodicarbonic acid, O,O'-dicyclohexyldithioimidodicarbonic acid, and O,O'-norbornyldithioimidodicarbonic acid.

S Valence Stabilizer #5: Examples of 1,3-dithioketones (dithio-beta-ketonates), 1,3,5-trithioketones, bis(1,3-dithioketones), and poly(1,3-dithioketones) (S-S Bidentates, S-S Tridentates, S-S Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: hexafluoropentanedithione; 1,3-diphenyl-1,3-propanedithione; thiobenzoylthiopinacolone; dithiocyclohexoxymethane; diphenylpentanetrithionate; tetramethylnonanetrithionate; hexafluoroheptanetrithionate; trifluoroheptanetrithionate; 1-(2-thienyl)-1,3-butanedithione, 1-(2-naphthyl)-1,3-butanedithione, trifluorothioacetylthiocamphor; and 1,3-indandithione.

S Valence Stabilizer #6: Examples of 1,2-dithioketones (dithiolenes, dithio-alpha-ketonates), 1,2,3-trithioketones, dithiotropolonates, o-dithioquinones, bis(1,2-dithioketones), and poly(1,2-dithioketones) (S-S Bidentates, S-S Tridentates, S-S Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dithiotropolone; 1,2-dithiobenzoquinone (o-dithioquinone)(o-benzenedithiolate)(bdt); di-tert-butyl-1,2-dithiobenzoquinone; hexafluoro-1,2-dithiobenzoquinone; 1,2-dithionaphthoquinone; 9,10-dithiophenanthroquinone; ethylenedithiolene (edt); maleonitriledithiolene (mnt); trifluoromethyldithiolene (tfd); carbomethoxydithiolene (cmt); trithionedithiolene (dmit); toluenedithiolate (tdt); dithiomanaldehyde (propenethionethiolate)(ptt); dithioacetylacetone (SacSac); dijulolidinedithiolene; 2,3-piperazinedithiolate; di(4-aminophenyl)dithiolene; dimercaptoisotriethione (dmit); (4-octylphenyl)dithiolene; benzenetetrathiol; tetrathiosquaric acid; trithiodeltic acid; pentathiocroconic acid; dithiocroconic acid; hexathiorhodizonic acid; dithiorhodizonic acid; ethylenetetrathiol; trans-butadienetetrathiolate; tetrathiooxalic acid; 1,2-

indandithione; naphthothioquinone; acenapthenethioquinone; aceanthrenethioquinone; and indole-2,3-dithione (thioisatin).

S Valence Stabilizer #7: Examples of dithiomalonamides (dithiomalonodiamides),
5 bis(dithiomalonamides), and polydithiomalonamides (S-S Bidentates, S-S Tridentates, S-S Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dithiomalonamide, N-phenyldithiomalonamide, N-
benzyldithiomalonamide, N-pentafluorophenyldithiomalonamide, N-
cyclohexyldithiomalonamide, N-norbornyldithiomalonamide, N,N'-diphenyldithiomalonamide,
10 N,N'-dibenzylidithiomalonamide, N,N'-dipentafluorophenyldithiomalonamide, N,N'-
dicyclohexyldithiomalonamide, and N,N'-norbornyldithiomalonamide.

S Valence Stabilizer #8: Examples of 2-thioacylthioacetamides, bis(2-thioacylthioacetamides), and poly(2-thioacylthioacetamides) (S-S Bidentates, S-S Tridentates, S-S Tetridentates) that
15 meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-thioacetothioacetamide, N-phenyl-2-thioacetothioacetamide, N-pentafluorophenyl-
2-thioacetothioacetamide, N-benzyl-2-thioacetothioacetamide, N-cyclohexyl-2-
thioacetothioacetamide, N-norbornyl-2-thioacetothioacetamide, N-phenyl-2-
thiobenzothioacetamide, N-pentafluorophenyl-2-pentafluorothiobenzothioacetamide, and N-
20 cyclohexyl-2-thiocyclohexothioacetamide.

S Valence Stabilizer #9: Examples of dithioacyl sulfides, bis(dithioacyl sulfides), and poly(dithioacyl sulfides), (S-S Bidentates, S-S Tridentates, S-S Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to:
25 dithioacetyl sulfide; dithiopropanoyl sulfide; dithiobenzoyl sulfide; and dithiopentafluorobenzoyl sulfide.

S Valence Stabilizer #10: Examples of trithiodicarbonic diamides, bis(trithiodicarbonic diamides), and poly(trithiodicarbonic diamides) (S-S Bidentates, S-S Tridentates, S-S Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: trithiodicarbonic diamide; N-phenyltrithiodicarbonic diamide; N-
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pentafluorophenyltrithiodicarbonic diamide; N-benzyltrithiodicarbonic diamide; N-cyclohexyltrithiodicarbonic diamide; N-norbornyltrithiodicarbonic diamide; N,N'-diphenyltrithiodicarbonic diamide; N,N'-dipentafluorophenyltrithiodicarbonic diamide; N,N'-dibenzyltrithiodicarbonic diamide; N,N'-dicyclohexyltrithiodicarbonic diamide; and N,N'-
5 dinorbornyltrithiodicarbonic diamide.

S Valence Stabilizer #11: Examples of pentathio-, tetrathio-, or trithiodicarbonic acids, bis(pentathio-, tetrathio-, or trithiodicarbonic acids), poly(pentathio-, tetrathio-, or trithiodicarbonic acids), and derivatives thereof (S-S Bidentates, S-S Tridentates, S-S Tetradentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: pentathiodicarbonic acid, tetrathiodicarbonic acid, trithiodicarbonic acid, O-phenyltrithiodicarbonic acid, O-benzyltrithiodicarbonic acid, O-cyclohexyltrithiodicarbonic acid, O-norbornyltrithiodicarbonic acid, O,O'-diphenyltrithiodicarbonic acid, O,O'-dibenzyltrithiodicarbonic acid, O,O'-
10 dicyclohexyltrithiodicarbonic acid, and O,O'-dinorbornyltrithiodicarbonic acid.
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S Valence Stabilizer #12: Examples of dithiohypophosphoric acids, bis(dithiohypophosphoric acids), poly(dithiohypophosphoric acids), and derivatives thereof (S-S Bidentates, S-S Tridentates, S-S Tetradentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dithiohypophosphoric acid, methyldithiohypophosphoric acid, isopropyldithiohypophosphoric acid, tert-butyldithiohypophosphoric acid, phenyldithiohypophosphoric acid, pentafluorophenyldithiohypophosphoric acid, benzylidithiohypophosphoric acid, cyclohexyldithiohypophosphoric acid, norbornyldithiohypophosphoric acid,
20 dimethyldithiohypophosphoric acid, diisopropyldithiohypophosphoric acid, di-tert-butyldithiohypophosphoric acid, diphenyldithiohypophosphoric acid, di-
25 pentafluorophenyldithiohypophosphoric acid, dibenzylidithiohypophosphoric acid, dicyclohexyldithiohypophosphoric acid, and dinorbornyldithiohypophosphoric acid.

S Valence Stabilizer #13: Examples of dithiohypophosphoramides, bis(dithiohypophosphoramides), and poly(dithiohypophosphoramides) (S-S Bidentates, S-S

Tridentates, S-S Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dithiohypophosphoramide, N-methyldithiohypophosphoramide, N-isopropyldithiohypophosphoramide, N-tert-butylidithiohypophosphoramide, N-phenyldithiohypophosphoramide, N-pentafluorophenyldithiohypophosphoramide, N-benzyldithiohypophosphoramide, N-cyclohexyldithiohypophosphoramide, N-norbornyldithiohypophosphoramide, N,N”-dimethyldithiohypophosphoramide, N,N”-diisopropyldithiohypophosphoramide, N,N”-di-tert-butylidithiohypophosphoramide, N,N”-diphenyldithiohypophosphoramide, N,N”-di-pentafluorophenyldithiohypophosphoramide, N,N”-dibenzylidithiohypophosphoramide, N,N”-dicyclohexyldithiohypophosphoramide, and N,N”-dinorbornyldithiohypophosphoramide.

S Valence Stabilizer #14: Examples of dithioimidodiphosphoric acids, dithiohydrazidodiphosphoric acids, bis(dithioimidodiphosphoric acids), bis(dithiohydrazidodiphosphoric acids), poly(dithioimidodiphosphoric acids), poly(dithiohydrazidodiphosphoric acids), and derivatives thereof (S-S Bidentates, S-S Tridentates, S-S Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dithioimidodiphosphoric acid, methyldithioimidodiphosphoric acid, isopropyldithioimidodiphosphoric acid, tert-butylidithioimidodiphosphoric acid, phenyldithioimidodiphosphoric acid, pentafluorophenyldithioimidodiphosphoric acid, benzyldithioimidodiphosphoric acid, cyclohexyldithioimidodiphosphoric acid, norbornyldithioimidodiphosphoric acid, dimethyldithioimidodiphosphoric acid, diisopropyldithioimidodiphosphoric acid, di-tert-butylidithioimidodiphosphoric acid, diphenyldithioimidodiphosphoric acid, di-pentafluorophenyldithioimidodiphosphoric acid, dibenzylidithioimidodiphosphoric acid, dicyclohexyldithioimidodiphosphoric acid, and dinorbornyldithioimidodiphosphoric acid.

S Valence Stabilizer #15: Examples of dithioimidodiphosphoramides, dithiohydrazidodiphosphoramides, bis(dithioimidodiphosphoramides), bis(dithiohydrazidodiphosphoramides), poly(dithioimidodiphosphoramides), and poly(dithiohydrazidodiphosphoramides) (S-S Bidentates, S-S Tridentates, S-S Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not

limited to: dithioimidodiphosphoramides, N-methyldithioimidodiphosphoramides, N-isopropyldithioimidodiphosphoramides, N-tert-butyldithioimidodiphosphoramides, N-phenyldithioimidodiphosphoramides, N-pentafluorophenyldithioimidodiphosphoramides, N-benzylidithioimidodiphosphoramides, N-cyclohexyldithioimidodiphosphoramides, N-norbornyldithioimidodiphosphoramides, N,N''-dimethyldithioimidodiphosphoramides, N,N''-diisopropyldithioimidodiphosphoramides, N,N''-di-tert-butyldithioimidodiphosphoramides, N,N''-diphenyldithioimidodiphosphoramides, N,N''-di-pentafluorophenyldithioimidodiphosphoramides, N,N''-dibenzylidithioimidodiphosphoramides, N,N''-dicyclohexyldithioimidodiphosphoramides, and N,N''-dinorbornyldithioimidodiphosphoramides.

S Valence Stabilizer #16: Examples of dithiodiphosphoramides, bis(dithiodiphosphoramides), and poly(dithiodiphosphoramides) (S-S Bidentates, S-S Tridentates, S-S Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dithiodiphosphoramides, N-methyldithiodiphosphoramides, N-isopropyldithiodiphosphoramides, N-tert-butyldithiodiphosphoramides, N-phenyldithiodiphosphoramides, N-pentafluorophenyldithiodiphosphoramides, N-benzylidithiodiphosphoramides, N-cyclohexyldithiodiphosphoramides, N-norbornyldithiodiphosphoramides, N,N''-dimethyldithiodiphosphoramides, N,N''-diisopropyldithiodiphosphoramides, N,N''-di-tert-butyldithiodiphosphoramides, N,N''-diphenyldithiodiphosphoramides, N,N''-di-pentafluorophenyldithiodiphosphoramides, N,N''-dibenzylidithiodiphosphoramides, N,N''-dicyclohexyldithiodiphosphoramides, and N,N''-dinorbornyldithiodiphosphoramides.

S Valence Stabilizer #17: Examples of dithiodiphosphoric acids, bis(dithiodiphosphoric acids), poly(dithiodiphosphoric acids), and derivatives thereof (S-S Bidentates, S-S Tridentates, S-S Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dithiodiphosphoric acid, methyldithiodiphosphoric acid, isopropyldithiodiphosphoric acid, tert-butyldithiodiphosphoric acid, phenyldithiodiphosphoric acid, pentafluorophenyldithiodiphosphoric acid, benzylidithiodiphosphoric acid, cyclohexyldithiodiphosphoric acid, norbornyldithiodiphosphoric acid,

dimethyldithiodiphosphoric acid, diisopropyldithiodiphosphoric acid, di-tert-butylidithiodiphosphoric acid, diphenyldithiodiphosphoric acid, di-pentafluorophenyldithiodiphosphoric acid, dibenzylidithiodiphosphoric acid, dicyclohexyldithiodiphosphoric acid, and dinorbornyldithiodiphosphoric acid.

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S Valence Stabilizer #18: Examples of trithiophosphoric acids (phosphorotrithioic acids), bis(trithiophosphoric acids), poly(trithiophosphoric acids), and derivatives thereof (S-S Bidentates, S-S Tridentates, S-S Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: trithiophosphoric acid, O-phenyltrithiophosphoric acid, O-benzyltrithiophosphoric acid, O-cyclohexyltrithiophosphoric acid, O-norbornyltrithiophosphoric acid, O,S-diphenyltrithiophosphoric acid, O,S-dibenzyltrithiophosphoric acid, O,S-dicyclohexyltrithiophosphoric acid, and O,S-dinorbornyltrithiophosphoric acid.

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S Valence Stabilizer #19: Examples of dithiophosphoric acids (phosphorodithioic acids), bis(dithiophosphoric acids), poly(dithiophosphoric acids), and derivatives thereof (S-S Bidentates, S-S Tridentates, S-S Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dithiophosphoric acid, O-phenyldithiophosphoric acid, O-benzyldithiophosphoric acid, O-cyclohexyldithiophosphoric acid, O-norbornyldithiophosphoric acid, O,O-diphenyldithiophosphoric acid, O,O-dibenzylidithiophosphoric acid, O,O-dicyclohexyldithiophosphoric acid, and O,O-dinorbornyldithiophosphoric acid.

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S Valence Stabilizer #20: Examples of tetrathiophosphoric acids (phosphorotetrathioic acids), bis(tetrathiophosphoric acids), poly(tetrathiophosphoric acids), and derivatives thereof (S-S Bidentates, S-S Tridentates, S-S Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: tetrathiophosphoric acid, S-phenyltetrathiophosphoric acid, S-benzyltetrathiophosphoric acid, S-cyclohexyltetrathiophosphoric acid, S-norbornyltetrathiophosphoric acid, S,S-diphenyltetrathiophosphoric acid, S,S-dibenzyltetrathiophosphoric acid, S,S-dicyclohexyltetrathiophosphoric acid, and S,S-dinorbornyltetrathiophosphoric acid.

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S Valence Stabilizer #21: Examples of phosphoro(dithioperoxo)dithioic acids, bis[phosphoro(dithioperoxo)dithioic acids], poly[phosphoro(dithioperoxo)dithioic acids], and derivatives thereof (S-S Bidentates, S-S Tridentates, S-S Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to:
5 phosphoro(dithioperoxo)dithioic acid, O-phenylphosphoro(dithioperoxo)dithioic acid, O-benzylphosphoro(dithioperoxo)dithioic acid, O-cyclohexylphosphoro(dithioperoxo)dithioic acid, O-norbornylphosphoro(dithioperoxo)dithioic acid, O,S-diphenylphosphoro(dithioperoxo)dithioic acid, O,S-dibenzylphosphoro(dithioperoxo)dithioic acid, O,S-dicyclohexylphosphoro(dithioperoxo)dithioic acid, and O,S-10 dinorbornylphosphoro(dithioperoxo)dithioic acid.

S Valence Stabilizer #22: Examples of phosphoro(dithioperoxo)thioic acids, bis[phosphoro(dithioperoxo)thioic acids], poly[phosphoro(dithioperoxo)thioic acids], and derivatives thereof (S-S Bidentates, S-S Tridentates, S-S Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to:
15 phosphoro(dithioperoxo)thioic acid, O-phenylphosphoro(dithioperoxo)thioic acid, O-benzylphosphoro(dithioperoxo)thioic acid, O-cyclohexylphosphoro(dithioperoxo)thioic acid, O-norbornylphosphoro(dithioperoxo)thioic acid, O,S-diphenylphosphoro(dithioperoxo)thioic acid, O,S-dibenzylphosphoro(dithioperoxo)thioic acid, O,S-dicyclohexylphosphoro(dithioperoxo)thioic acid, and O,S-20 dinorbornylphosphoro(dithioperoxo)thioic acid.

S Valence Stabilizer #23: Examples of phosphoro(dithioperoxo)trithioic acids, bis[phosphoro(dithioperoxo)trithioic acids], poly[phosphoro(dithioperoxo)trithioic acids], and derivatives thereof (S-S Bidentates, S-S Tridentates, S-S Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to:
25 phosphoro(dithioperoxo)trithioic acid, O-phenylphosphoro(dithioperoxo)trithioic acid, O-benzylphosphoro(dithioperoxo)trithioic acid, O-cyclohexylphosphoro(dithioperoxo)trithioic acid, O-norbornylphosphoro(dithioperoxo)trithioic acid, O,S-diphenylphosphoro(dithioperoxo)trithioic acid, O,S-30

acid, O,S-dicyclohexylphosphoro(dithioperoxo)trithioic acid, and O,S-dinorbornylphosphoro(dithioperoxo)trithioic acid.

S Valence Stabilizer #24: Examples of beta-mercaptopthioketones, beta-mercaptopthioaldehydes, bis(beta-mercaptopthioketones), bis(beta-mercaptopthioaldehydes), poly(beta-mercaptopthioketones), and poly(beta-mercaptopthioaldehydes) (S-S Bidentates, S-S Tridentates, S-S Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 4-mercaptopentan-2-thione; 1,3-diphenyl-3-mercaptopropanethioaldehyde; 1,3-dibenzyl-3-mercaptopropanethioaldehyde; 1,3-dicyclohexyl-3-mercaptopropanethioaldehyde; 1,3-dinorbornyl-3-mercaptopropanethioaldehyde; 1,3-di(2-thienyl)-3-mercaptopropanethioaldehyde; 1,3-di(2-furyl)-3-mercaptopropanethioaldehyde; o-mercaptopthioacetophenone; 5-mercapto-1,4-dithionaphthoquinone; 1-mercaptopthioacridone; 1-mercaptodithioanthraquinone; 1,8-dimercaptodithioanthraquinone; and beta-mercaptopthiobenzophenone.

S Valence Stabilizer #25: Examples of N-(aminomethylthiol)thioureas [N-(aminomercaptomethyl)thioureas], bis[N-(aminomethylthiol)thioureas], and poly[N-(aminomethylthiol)thioureas] (S-S Bidentates, S-S Tridentates, S-S Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: N’-(aminomercaptomethyl)thiourea; N,N”-dimethyl-N’-(aminomercaptomethyl)thiourea; N,N’-diethyl-N’-(aminomercaptomethyl)thiourea; N,N”-isopropyl-N’-(aminomercaptomethyl)thiourea; N,N”-diphenyl-N’-(aminomercaptomethyl)thiourea; N,N”-dibenzyl-N’-(aminomercaptomethyl)thiourea; N,N”-dicyclohexyl-N’-(aminomercaptomethyl)thiourea; and N,N”-dinorbornyl-N’-(aminomercaptomethyl)thiourea.

S Valence Stabilizer #26: Examples of dithioxamides, bis(dithioxamides), and poly(dithioxamides) (S-S Bidentates, S-S Tridentates, S-S Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dithioxamide (rubenic acid), N-methyldithioxamide; N-ethyldithioxamide; N-isopropyldithioxamide; N-phenyldithioxamide; N-benzyldithioxamide; N-cyclohexyldithioxamide; N-norbornyldithioxamide; N,N’-dimethyldithioxamide; N,N’-

diethyldithioxamide; N,N'-diisopropylidithioxamide; N,N'-diphenylidithioxamide; N,N'-dibenzylidithioxamide; N,N'-dicyclohexylidithioxamide; and N,N'-dinorbornylidithioxamide.

S Valence Stabilizer #27: Examples of 1,1-dithiolates, bis(1,1-dithiolates), and poly(1,1-dithiolates) (S-S Bidentates and S-S Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 1,1-dicyano-2,2-ethylene dithiolate (i-mnt); 1,1-dicarboalkoxy-2,2-ethylene dithiolate (DED); 1,1-di(trifluoromethyl)-2,2-ethylene dithiolate; 1,1-di(pentafluorophenyl)-2,2-ethylene dithiolate; 1-pentamethylene-2,2-ethylene dithiolate; and 1-nitroethylene dithiolate.

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S Valence Stabilizer #28: Examples of dithiomonocarboxylic acids, tri- and tetrathiodicarboxylic Acids, bis(dithiomonocarboxylic acids), bis(tri- and tetrathiodicarboxylic acids), poly(dithiomonocarboxylic acids), poly(tri- and tetrathiodicarboxylic acids), and derivatives thereof (S-S Bidentates and S-S Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dithioacetic acid; dithiopropionic acid; dithiobenzoic acid (dtb); dithiophenylacetic acid (dtpa); dithiocyclohexanoic acid; dithiofuroic acid; dithionaphthoic acid; phenyl dithioacetate; phenyl dithiopropionate; phenyl dithiobenzoate; phenyl dithiocyclohexanoate; phenyl dithiofuroate; phenyl dithionaphthoate; tetrathiooxalic acid; tetrathiomalonic acid; tetrathiosuccinic acid; trithiooxalic acid; trithiomalonic acid; trithiosuccinic acid; diphenyl tetrathiooxalate; diphenyl tetrathiomalonate; diphenyl tetrathiosuccinate; diphenyl trithiooxalate; diphenyl trithiomalonate; diphenyl trithiosuccinate; pyridine dithiocarboxylic acid; pyrrole dithiocarboxylic acid; thiophene dithiocarboxylic acid; dithionaphthoic acid; and tetrathiocamphonic acid.

S Valence Stabilizer #29: Examples of perthiomonocarboxylic acids, perthiodicarboxylic acids, bis(perthiomonocarboxylic acids), bis(perthiodicarboxylic acids), poly(perthiomonocarboxylic acids), poly(perthiodicarboxylic acids), and derivatives thereof (S-S Bidentates and S-S Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: perthioacetic acid; perthiopropionic acid; perthiobenzoic acid; perthiophenylacetic acid; perthiocyclohexanoic acid; perthiofuroic acid; perthionaphthoic acid; phenyl perthioacetate; phenyl perthiopropionate; phenyl perthiobenzoate; phenyl

perthiocyclohexanoate; phenyl perthiofuroate; phenyl perthionaphthoate; perthiooxalic acid; perthiomalonic acid; perthiosuccinic acid; diphenyl perthioxalate; diphenyl perthiomalonate; diphenyl perthiosuccinate; dithiole-3-thione (dithione-3-thione); and benzodithiole-3-thione (benzodithione-3-thione).

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S Valence Stabilizer #30: Examples of dithiocarbonates, trithiocarbonates, perthiocarbonates, bis(dithiocarbonates), bis(trithiocarbonates), and bis(perthiocarbonates) (S-S Bidentates and S-S Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: S,S-diethyldithiocarbonate; S,S-diisopropylidithiocarbonate; S,S-diphenyldithiocarbonate; S,S-dibenzylidithiocarbonate; S,S-dicyclohexyldithiocarbonate; S,S-dinorbornyldithiocarbonate; diethyltrithiocarbonate; diisopropyltrithiocarbonate; diphenyltrithiocarbonate; dibenzyltrithiocarbonate; dicyclohexyltrithiocarbonate; and dinorbornyltrithiocarbonate.

15 S Valence Stabilizer #31: Examples of dithiocarbamates, bis(dithiocarbamates), and poly(dithiocarbamates) (including N-hydroxydithiocarbamates and N-mercaptodithiocarbamates) (S-S Bidentates, S-S Tridentates, and S-S Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dimethyldithiocarbamate (dmdtc); di(trifluorodimethyl)dithiocarbamate; diethyldithiocarbamate (dedtc);
20 dipropyldithiocarbamate; diisopropyldithiocarbamate; dibutyldithiocarbamate; ditertbutyldithiocarbamate; dicyanamidotriethyldithiocarbamate; azidothioformates; diphenyldithiocarbamate; di(pentafluorophenyl)dithiocarbamate; dibenzylidithiocarbamate; dinaphthyldithiocarbamate; dicyclohexyldithiocarbamate; dinorbornyldithiocarbamate; diadamantyldithiocarbamate; pyrrolidinodithiocarbamate (pyrdtc); piperidinodithiocarbamate
25 (pipdtc); morpholinodithiocarbamate (mordtc); thiamorpholinodithiocarbamate; 3-pyrrolinodithiocarbamate; pyrrolodithiocarbamate; oxazolodithiocarbamate; isoxazolodithiocarbamate; thiazolodithiocarbamate; isothiazolodithiocarbamate; indolodithiocarbamate; carbazolodithiocarbamate; pyrazolinodithiocarbamate; imidazolinodithiocarbamate; pyrazolodithiocarbamate; imidazolodithiocarbamate; indazolodithiocarbamate; and triazolodithiocarbamate.

S Valence Stabilizer #32: Examples of dithiocarbazates (dithiocarbazides), bis(dithiocarbazates), and poly(dithiocarbazates) (S-S Bidentates, S-S Tridentates, and S-S Tetridentates; or possibly N-S Bidentates, N-S Tridentates, and N-S Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: N,N'-

5 dimethyldithiocarbazate; N,N'-di(trifluoromethyl)dithiocarbazate; N,N'-diethyldithiocarbazate; N,N'-diphenyldithiocarbazate; N,N'-dibenzylidithiocarbazate; N,N'-di(pentafluorophenyl)dithiocarbazate; N,N'-dicyclohexyldithiocarbazate; and N,N'-dinorbornyldithiocarbazate.

10 S Valence Stabilizer #33: Examples of thiocyanate ligands (S monodentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: thiocyanate (-SCN).

O Valence Stabilizer #1: Examples of biurets (imidodicarbonic diamides), isobiurets, biureas, triurets, triureas, bis(biurets), bis(isobiurets), bis(biureas), poly(biurets), poly(isobiurets), and poly(biureas) (O-O Bidentates, O-O Tridentates, O-O Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: biuret, isobiuret, biurea, triuret, triurea, nitrobiuret, dinitrobiuret, aminobiuret, diaminobiuret, oxybiuret, dioxybiuret, cyanobiuret, methylbiuret, ethylbiuret, isopropylbiuret, phenylbiuret, benzylbiuret, cyclohexylbiuret, norbornylbiuret, adamantlylbiuret, dimethylbiuret, diethylbiuret, diisopropylbiuret, diphenylbiuret, dibenzylbiuret, dicyclohexylbiuret, dinorbornylbiuret, and diadamantlylbiuret.

25 O Valence Stabilizer #2: Examples of acylureas, aroylureas, bis(acylureas), bis(aroylureas), poly(acylureas), and poly(aroylureas) (O-O Bidentates, O-O Tridentates, O-O Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: formylurea, acetylurea, benzoylurea, cyclohexoylurea, pentafluorobenzoylurea, N-methylacetylurea, N-phenylbenzoylurea, and N-cyclohexylcyclohexoylurea.

30 O Valence Stabilizer #3: Examples of imidodialdehydes, hydrazidodialdehydes (acyl hydrazides), bis(imidodialdehydes), bis(hydrazidodialdehydes), poly(imidodialdehydes), and

poly(hydrazidodialdehydes) (O-O Bidentates, O-O Tridentates, O-O Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diacetamide, dipropanamide, dibutanamide, dibenzamide, and dicyclohexamide.

- 5 O Valence Stabilizer #4: Examples of imidodicarbonic acids, hydrazidodicarbonic acids, bis(imidodicarbonic acids), bis(hydrazidodicarbonic acids), poly(imidodicarbonic acids), poly(hydrazidodicarbonic acids) and derivatives thereof (O-O Bidentates, O-O Tridentates, O-O Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: imidodicarbonic acid, hydrazidodicarbonic acid, O-phenylimidodicarbonic acid, O-benzylimidodicarbonic acid, O-cyclohexylimidodicarbonic acid, O-norbornylimidodicarbonic acid, O,O'-diphenylimidodicarbonic acid, O,O'-dibenzylimidodicarbonic acid, O,O'-dicyclohexylimidodicarbonic acid, and O,O'-dinorbornylimidodicarbonic acid.
- 10 O Valence Stabilizer #5: Examples of imidodisulfamic acid, imidodisulfuric acid, bis(imidodisulfamic acid), bis(imidodisulfuric acid), poly(imidodisulfamic acid), and poly(imidodisulfuric acid) and derivatives thereof (O-O Bidentates, O-O Tridentates, O-O Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: imidodisulfamic acid, imidodisulfuric acid, N-phenylimidodisulfamic acid, N-benzylimidodisulfamic acid, N-cyclohexylimidodisulfamic acid, N-norbornylimidodisulfamic acid, N,N'-diphenylimidodisulfamic acid, N,N'-dibenzylimidodisulfamic acid, N,N'-dicyclohexylimidodisulfamic acid, and N,N'-norbornylimidodisulfamic acid.
- 15 O Valence Stabilizer #6: Examples of 1,3-diketones (beta-diketonates), 1,3,5-triketones, bis(1,3-diketones), and poly(1,3-diketones), all with a molecular weight greater than 125 (O-O Bidentates, O-O Tridentates, O-O Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: hexafluoropentanedione; dibenzoylmethane (1,3-diphenyl-1,3-propanedione); benzoylpinacolone; dicyclohexoxymethane; diphenylpentanetrionate; dibenzoylacetone; benzoylacetylacetone; dibenzoylacetylacetone;
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tetramethylnonanetrionate; hexafluoroheptanetrionate; trifluoroheptanetrionate; trifluoroacetylcamphor (facam); and
1,3-indandione.

5 O Valence Stabilizer #7: Examples of 1,2-diketones (alpha-diketonates), 1,2,3-triketones, tropolonates, o-quinones, bis(1,2-diketones), and poly(1,2-diketones), all with a molecular weight greater than 100 (O-O Bidentates, O-O Tridentates, O-O Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to:
10 tropolone; 1,2-benzoquinone (o-quinone); di-tert-butyl-1,2-benzoquinone; hexafluoro-1,2-benzoquinone; 1,2-naphthoquinone; 9,10-phenanthroquinone; and
1,2-indandione.

15 O Valence Stabilizer #8: Examples of malonamides (malonodiamides), bis(malonamides), and polymalonamides (O-O Bidentates, O-O Tridentates, O-O Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to:
malonamide, N-phenylmalonamide, N-benzylmalonamide, N-pentafluorophenylmalonamide, N-cyclohexylmalonamide, N-norbornylmalonamide, N,N'-diphenylmalonamide, N,N'-dibenzylmalonamide, N,N'-dipentafluorophenylmalonamide, N,N'-dicyclohexylmalonamide, and N,N'-norbornylmalonamide.
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25 O Valence Stabilizer #9: Examples of 2-acylacetamides, bis(2-acylacetamides), and poly(2-acylacetamides) (O-O Bidentates, O-O Tridentates, O-O Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to:
2-acetoacetamide, N-phenyl-2-acetoacetamide, N-pentafluorophenyl-2-acetoacetamide, N-benzyl-2-acetoacetamide, N-cyclohexyl-2-acetoacetamide, N-norbornyl-2-acetoacetamide, N-phenyl-2-benzoacetamide, N-pentafluorophenyl-2-pentafluorobenzoacetamide, and N-cyclohexyl-2-cyclohexoacetamide.

30 O Valence Stabilizer #10: Examples of monothiodicarbonic diamides, bis(monothiodicarbonic diamides), and poly(monothiodicarbonic diamides) (O-O Bidentates, O-O Tridentates, O-O Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴

include, but are not limited to: monothiodicarbonic diamide; N-phenylmonothiodicarbonic diamide; N-pentafluorophenylmonothiodicarbonic diamide; N-benzylmonothiodicarbonic diamide; N-cyclohexylmonothiodicarbonic diamide; N-norbornylmonothiodicarbonic diamide; N,N'-diphenylmonothiodicarbonic diamide; N,N'-dipentafluorophenylmonothiodicarbonic diamide; N,N'-dibenzylmonothiodicarbonic diamide; N,N'-dicyclohexylmonothiodicarbonic diamide; and N,N'-dinorbornylmonothiodicarbonic diamide.

5 O Valence Stabilizer #11: Examples of monothiodicarbonic acids, bis(monothiodicarbonic acids), poly(monothiodicarbonic acids), and derivatives thereof (O-O Bidentates, O-O Tridentates, O-O Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: monothiodicarbonic acid, O-phenylmonothiodicarbonic acid, O-benzylmonothiodicarbonic acid, O-cyclohexylmonothiodicarbonic acid, O-norbornylmonothiodicarbonic acid, O,O'-diphenylmonothiodicarbonic acid, O,O'-dibenzylmonothiodicarbonic acid, O,O'-dicyclohexylmonothiodicarbonic acid, and O,O'-dinorbornylmonothiodicarbonic acid.

10 O Valence Stabilizer #12: Examples of trithionic acid, bis(trithionic acid), poly(trithionic acid), and derivatives thereof (O-O Bidentates, O-O Tridentates, O-O Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diphenyl trithionate, dipentafluorodiphenyl trithionate, dicyclohexyl trithionate, and dinorbornyl trithionate.

15 O Valence Stabilizer #13: Examples of hypophosphoric acids, bis(hypophosphoric acids), and poly(hypophosphoric acids), and derivatives thereof (O-O Bidentates, O-O Tridentates, O-O Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: hypophosphoric acid, O-methylhypophosphoric acid, O-isopropylhypophosphoric acid, O-tert-butylhypophosphoric acid, O-phenylhypophosphoric acid, O-pentafluorophenylhypophosphoric acid, O-benzylhypophosphoric acid, O-cyclohexylhypophosphoric acid, O-norbornylhypophosphoric acid, O,O''-dimethylhypophosphoric acid, O,O''-diisopropylhypophosphoric acid, O,O''-di-tert-butylhypophosphoric acid, O,O''-diphenylhypophosphoric acid, O,O''-di-

pentafluorophenylhypophosphoric acid, O,O"-dibenzylhypophosphoric acid, O,O"-dicyclohexylhypophosphoric acid, and O,O"-dinorbornylhypophosphoric acid.

O Valence Stabilizer #14: Examples of hypophosphoramides, bis(hypophosphoramides), and poly(hypophosphoramides) (O-O Bidentates, O-O Tridentates, O-O Tetridentates) that meet the requirements for use as "wide band" valence stabilizers for Ce⁺⁴ include, but are not limited to: hypophosphoramide, N-methylhypophosphoramide, N-isopropylhypophosphoramide, N-tert-butylhypophosphoramide, N-phenylhypophosphoramide, N-pentafluorophenylhypophosphoramide, N-benzylhypophosphoramide, N-cyclohexylhypophosphoramide, N-norbornylhypophosphoramide, N,N"-dimethylhypophosphoramide, N,N"-diisopropylhypophosphoramide, N,N"-di-tert-butylhypophosphoramide, N,N"-diphenylhypophosphoramide, N,N"-dipentafluorophenylhypophosphoramide, N,N"-dibenzylhypophosphoramide, N,N"-dicyclohexylhypophosphoramide, and N,N"-dinorbornylhypophosphoramide.

O Valence Stabilizer #15: Examples of imidodiphosphoric acids, hydrazidodiphosphoric acids, bis(imidodiphosphoric acids), bis(hydrazidodiphosphoric acids), poly(imidodiphosphoric acids), poly(hydrazidodiphosphoric acids), and derivatives thereof (O-O Bidentates, O-O Tridentates, O-O Tetridentates) that meet the requirements for use as "wide band" valence stabilizers for Ce⁺⁴ include, but are not limited to: imidodiphosphoric acid, methylimidodiphosphoric acid, isopropylimidodiphosphoric acid, tert-butylimidodiphosphoric acid, phenylimidodiphosphoric acid, pentafluorophenylimidodiphosphoric acid, benzylimidodiphosphoric acid, cyclohexylimidodiphosphoric acid, norbornylimidodiphosphoric acid, dimethylimidodiphosphoric acid, diisopropylimidodiphosphoric acid, di-tert-butylimidodiphosphoric acid, diphenylimidodiphosphoric acid, di-pentafluorophenylimidodiphosphoric acid, dibenzylimidodiphosphoric acid, dicyclohexylimidodiphosphoric acid, and dinorbornylimidodiphosphoric acid.

O Valence Stabilizer #16: Examples of imidodiphosphoramides, hydrazidodiphosphoramides, bis(imidodiphosphoramides), bis(hydrazidodiphosphoramides), poly(imidodiphosphoramides), and poly(hydrazidodiphosphoramides) (O-O Bidentates, O-O Tridentates, O-O Tetridentates)

that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: imidodiphosphoramide, N-methylimidodiphosphoramide, N-isopropylimidodiphosphoramide, N-tert-butylimidodiphosphoramide, N-phenylimidodiphosphoramide, N-pentafluorophenylimidodiphosphoramide, N-benzylimidodiphosphoramide, N-cyclohexylimidodiphosphoramide, N-norbornylimidodiphosphoramide, N,N''-dimethylimidodiphosphoramide, N,N''-diisopropylimidodiphosphoramide, N,N''-di-tert-butylimidodiphosphoramide, N,N''-diphenylimidodiphosphoramide, N,N''-di-pentafluorophenylimidodiphosphoramide, N,N''-dibenzylimidodiphosphoramide, N,N''-dicyclohexylimidodiphosphoramide, and N,N''-dinorbornylimidodiphosphoramide.

O Valence Stabilizer #17: Examples of diphosphoramides, bis(diphosphoramides), and poly(diphosphoramides) (O-O Bidentates, O-O Tridentates, O-O Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to:

diphosphoramide, N-methyldiphosphoramide, N-isopropyldiphosphoramide, N-tert-butyldiphosphoramide, N-phenyldiphosphoramide, N-pentafluorophenyldiphosphoramide, N-benzyldiphosphoramide, N-cyclohexyldiphosphoramide, N-norbornyldiphosphoramide, N,N''-dimethyldiphosphoramide, N,N''-diisopropyldiphosphoramide, N,N''-di-tert-butyldiphosphoramide, N,N''-diphenyldiphosphoramide, N,N''-di-pentafluorophenyldiphosphoramide, N,N''-dibenzylidiphosphoramide, N,N''-dicyclohexyldiphosphoramide, and N,N''-dinorbornyldiphosphoramide.

O Valence Stabilizer #18: Examples of beta-hydroxyketones, beta-hydroxyaldehydes, bis(beta-hydroxyketones), bis(beta-hydroxyaldehydes), poly(beta-hydroxyketones), and poly(beta-hydroxyaldehydes) (O-O Bidentates, O-O Tridentates, O-O Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to:

4-hydroxypentan-2-one; 1,3-diphenyl-3-hydroxypropanal; 1,3-dibenzyl-3-hydroxypropanal; 1,3-dicyclohexyl-3-hydroxypropanal; 1,3-dinorbornyl-3-hydroxypropanal; 1,3-di(2-thienyl)-3-hydroxypropanal; 1,3-di(2-furyl)-3-hydroxypropanal; o-hydroxyacetophenone; juglone; alizarin; 1-hydroxyanthraquinone; 1,8-hydroxyanthraquinone; 1-hydroxyacridone; and beta-hydroxybenzophenone.

O Valence Stabilizer #19: Examples of oxamides, bis(oxamides), and poly(oxamides) (O-O Bidentates, O-O Tridentates, O-O Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: oxamide; N-methyloxamide; N-ethyloxamide; N-isopropylloxamide; N-phenyloxamide; N-benzyloxamide; N-cyclohexyloxamide; N-norbornyloxamide; N,N'-dimethyloxamide; N,N'-diethyloxamide; N,N'-diisopropylloxamide; N,N'-diphenyloxamide; N,N'-dibenzylloxamide; N,N'-dicyclohexyloxamide; and N,N'-dinorbornyloxamide.

O Valence Stabilizer #20: Examples of squaric acids and derivatives thereof (O-O Bidentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: deltic acid; squaric acid; croconic acid; and rhodizonic acid.

O Valence Stabilizer #21: Examples of dicarboxylic acids, bis(dicarboxylic acids), poly(dicarboxylic acids), and derivatives thereof (O-O Bidentates and O-O Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: oxalic acid; malonic acid; succinic acid; diphenyl oxalate; diphenyl malonate; and diphenyl succinate.

O Valence Stabilizer #22: Examples of carbonates and bis(carbonates) (O-O Bidentates and O-O Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: carbonate; bicarbonate; O,O-diethylcarbonate; diisopropylcarbonate; diphenylcarbonate; dibenzylcarbonate; dicyclohexylcarbonate; and dinorbornylcarbonate.

O Valence Stabilizer #23: Examples of carbamates, bis(carbamates), and poly(carbamates) (including N-hydroxycarbamates and N-mercaptocarbamates) (O-O Bidentates, O-O Tridentates, and O-O Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dimethylcarbamate (dmc); di(trifluorodimethyl)carbamate; ethyl carbamate; diethylcarbamate (dec); dipropylcarbamate; diisopropylcarbamate; dibutylcarbamate; ditertbutylcarbamate; dicyanamidocarbamate; diphenylcarbamate; di(pentafluorophenyl)carbamate; dibenzylcarbamate; dinaphthylcarbamate;

dicyclohexylcarbamate; dinorbornylcarbamate; diadamantylcarbamate; pyrrolidinocarbamate (pyrc); piperidinocarbamate (pipc); morpholinocarbamate (morc); thiamorpholinocarbamate; 3-pyrrolinocarbamate; pyrrolocarbamate; oxazolocarbamate; isoxazolocarbamate; thiazolocarbamate; isothiazolocarbamate; indolocarbamate; carbazolocarbamate; 5 pyrazolinocarbamate; imidazolinocarbamate; pyrazolocarbamate; imidazolocarbamate; indazolocarbamate; and triazolocarbamate.

O Valence Stabilizer #24: Examples of carbimates, bis(carbimates), and poly(carbimates) (O-O Bidentates, O-O Tridentates, and O-O Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: methylcarbimate; 10 trifluoromethylcarbimate; ethylcarbimate; propylcarbimate; isopropylcarbimate; butylcarbimate; tertbutylcarbimate; cyanocarbimate; cyanamidocarbimate; azidocarbimate; phenylcarbimate; pentafluorophenylcarbimate; benzylcarbimate; naphthylcarbimate; cyclohexylcarbimate; norbornylcarbimate; and adamantlycarbimate. [Note: carbimates tend to stabilize lower oxidation 15 states in metal ions.]

O Valence Stabilizer #25: Examples of N-(aminomethylol)ureas [N-(aminohydroxymethyl)ureas], bis[N-(aminomethylol)ureas], and poly[N-(aminomethylol)ureas] (O-O Bidentates, O-O Tridentates, O-O Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: N'-20 (aminohydroxymethyl)urea; N,N''-dimethyl-N'-(aminohydroxymethyl)urea; N,N'-diethyl-N'-(aminohydroxymethyl)urea; N,N''-isopropyl-N'-(aminohydroxymethyl)urea; N,N''-diphenyl-N'-(aminohydroxymethyl)urea; N,N''-dibenzyl-N'-(aminohydroxymethyl)urea; N,N''-dicyclohexyl-N'-(aminohydroxymethyl)urea; and N,N''-dinorbornyl-N'-(aminohydroxymethyl)urea.

O Valence Stabilizer #26: Examples of cyanate ligands (O monodentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: cyanate (-OCN).

30 N-S Valence Stabilizer #1: Examples of diformamidine disulfides (thioperoxydicarbonimidic diamides), thioperoxytricarbonimidic diamides, thioperoxytetracarbonimidic diamides,

bis(diformamidine disulfides), and poly(diformamidine disulfides) (N-S bidentates, N-N-S tridentates, or N-S tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diformamidine disulfide; 5 methyldiformamidine disulfide; ethyldiformamidine disulfide; isopropyldiformamidine disulfide; butyldiformamidine disulfide; benzylidiformamidine disulfide; phenyldiformamidine disulfide; tolyldiformamidine disulfide; naphthyldiformamidine disulfide; cyclohexyldiformamidine disulfide; norbornyldiformamidine disulfide; adamantlyldiformamidine disulfide; dimethyldiformamidine disulfide; diethyldiformamidine disulfide; diisopropyldiformamidine disulfide; dibutyldiformamidine disulfide; dibenzylidiformamidine disulfide; 10 diphenyldiformamidine disulfide; ditolyldiformamidine disulfide; dinaphthyldiformamidine disulfide; dicyclohexyldiformamidine disulfide; dinorbornyldiformamidine disulfide; diadamantlyldiformamidine disulfide; 2-S-amidinodisulfidothiazole; 2-S-amidinodisulfidooxazole; 2-S-amidinodisulfidoimidazole; 3-S-amidinodisulfidopyrazole; 3-S-amidinodisulfido-1,2,4-triazole; and 5-S-amidinodisulfidotetrazole.

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N-S Valence Stabilizer #2: Examples of S-amidinodithiocarbamates, bis(S-amidinodithiocarbamates), and poly(S-amidinodithiocarbamates) (N-S Bidentates and N-S Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: S-amidinodithiocarbamate; N-methyl-S-amidinodithiocarbamate; 20 N-ethyl-S-amidinodithiocarbamate; N-isopropyl-S-amidinodithiocarbamate; N-butyl-S-amidinodithiocarbamate; N-benzyl-S-amidinodithiocarbamate; N-phenyl-S-amidinodithiocarbamate; N-tolyl-S-amidinodithiocarbamate; N-naphthyl-S-amidinodithiocarbamate; N-cyclohexyl-S-amidinodithiocarbamate; N-norbornyl-S-amidinodithiocarbamate; N-adamantyl-S-amidinodithiocarbamate; N,N'-dimethyl-S-amidinodithiocarbamate; N,N'-diethyl-S-amidinodithiocarbamate; N,N'-diisopropyl-S-amidinodithiocarbamate; N,N'-dibutyl-S-amidinodithiocarbamate; N,N'-dibenzyl-S-amidinodithiocarbamate; N,N'-diphenyl-S-amidinodithiocarbamate; N,N'-ditolyl-S-amidinodithiocarbamate; N,N'-dinaphthyl-S-amidinodithiocarbamate; N,N'-dicyclohexyl-S-amidinodithiocarbamate; N,N'-dinorbornyl-S-amidinodithiocarbamate; N,N'-diadamantyl-S-amidinodithiocarbamate; ethylenebis(S-amidinodithiocarbamate); propylenebis(S-amidinodithiocarbamate); phenylenebis(S-amidinodithiocarbamate); piperazinebis(S-

amidinodithiocarbamate); oxalylbis(S-amidinodithiocarbamate); malonylbis(S-amidinodithiocarbamate); succinylbis(S-amidinodithiocarbamate); phthalylbis(S-amidinodithiocarbamate); 2-S-dithiocarbamatothiazole; 2-S-dithiocarbamatooxazole; 2-S-dithiocarbamatotimidazole; 3-S-dithiocarbamatopyrazole; 3-S-dithiocarbamato-1,2,4-triazole; 5 and 5-S-dithiocarbamatotetrazole.

N-S Valence Stabilizer #3: Examples of O-amidinothiocarbamates, bis(O-amidinothiocarbamates), and poly(O-amidinothiocarbamates) (N-S Bidentates and N-S Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: O-amidinothiocarbamate; N-methyl-O-amidinothiocarbamate; N-ethyl-O-amidinothiocarbamate; N-isopropyl-O-amidinothiocarbamate; N-butyl-O-amidinothiocarbamate; N-benzyl-O-amidinothiocarbamate; N-phenyl-O-amidinothiocarbamate; N-tolyl-O-amidinothiocarbamate; N-naphthyl-O-amidinothiocarbamate; N-cyclohexyl-O-amidinothiocarbamate; N-norbornyl-O-amidinothiocarbamate; N-adamantyl-O-amidinothiocarbamate; N,N'-dimethyl-O-amidinothiocarbamate; N,N'-diethyl-O-amidinothiocarbamate; N,N'-diisopropyl-O-amidinothiocarbamate; N,N'-dibutyl-O-amidinothiocarbamate; N,N'-dibenzyl-O-amidinothiocarbamate; N,N'-diphenyl-O-amidinothiocarbamate; N,N'-ditolyl-O-amidinothiocarbamate; N,N'-dinaphthyl-O-amidinothiocarbamate; N,N'-dicyclohexyl-O-amidinothiocarbamate; N,N'-dinorbornyl-O-amidinothiocarbamate; N,N'-diadamantyl-O-amidinothiocarbamate; ethylenebis(O-amidinothiocarbamate); propylenebis(O-amidinothiocarbamate); phenylenebis(O-amidinothiocarbamate); piperazinebis(O-amidinothiocarbamate); oxalylbis(O-amidinothiocarbamate); malonylbis(O-amidinothiocarbamate); succinylbis(O-amidinothiocarbamate); phthalylbis(O-amidinothiocarbamate); 2-O-monothiocarbamatothiazole; 2-O-monothiocarbamatooxazole; 2-O-monothiocarbamatotimidazole; 3-O-monothiocarbamatopyrazole; 3-O-monothiocarbamato-1,2,4-triazole; and 5-O-monothiocarbamatotetrazole.

N-S Valence Stabilizer #4: Examples of S-amidinoperoxythiocarbamates, bis(S-amidinoperoxythiocarbamates), and poly(S-amidinoperoxythiocarbamates) (N-S Bidentates and N-S Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴

include, but are not limited to: S-amidinoperoxythiocarbamate; N-methyl-S-amidinoperoxythiocarbamate; N-ethyl-S-amidinoperoxythiocarbamate; N-isopropyl-S-amidinoperoxythiocarbamate; N-butyl-S-amidinoperoxythiocarbamate; N-benzyl-S-amidinoperoxythiocarbamate; N-phenyl-S-amidinoperoxythiocarbamate; N-tolyl-S-amidinoperoxythiocarbamate; N-naphthyl-S-amidinoperoxythiocarbamate; N-cyclohexyl-S-amidinoperoxythiocarbamate; N-norbornyl-S-amidinoperoxythiocarbamate; N-adamantyl-S-amidinoperoxythiocarbamate; N,N'-dimethyl-S-amidinoperoxythiocarbamate; N,N'-diethyl-S-amidinoperoxythiocarbamate; N,N'-diisopropyl-S-amidinoperoxythiocarbamate; N,N'-dibutyl-S-amidinoperoxythiocarbamate; N,N'-dibenzyl-S-amidinoperoxythiocarbamate; N,N'-diphenyl-S-amidinoperoxythiocarbamate; N,N'-ditolyl-S-amidinoperoxythiocarbamate; N,N'-dinaphthyl-S-amidinoperoxythiocarbamate; N,N'-dicyclohexyl-S-amidinoperoxythiocarbamate; N,N'-dinorbornyl-S-amidinoperoxythiocarbamate; N,N'-diadamantyl-S-amidinoperoxythiocarbamate; ethylenebis(S-amidinoperoxythiocarbamate); propylenebis(S-amidinoperoxythiocarbamate); phenylenebis(S-amidinoperoxythiocarbamate); piperazinebis(S-amidinoperoxythiocarbamate); oxalylbis(S-amidinoperoxythiocarbamate); malonylbis(S-amidinoperoxythiocarbamate); succinylbis(S-amidinoperoxythiocarbamate); and phthalylbis(S-amidinoperoxythiocarbamate).

N-S Valence Stabilizer #5: Examples of phosphorimidothioic acid; phosphorimidodithioic acid; phosphorimidotriethioic acid; bis(phosphorimidothioic acid); bis(phosphorimidodithioic acid); bis(phosphorimidotriethioic acid); poly(phosphorimidothioic acid); poly(phosphorimidodithioic acid); poly(phosphorimidotriethioic acid); and derivatives thereof (N-S Bidentates and N-S Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: phosphorimidothioic acid; phosphorimidodithioic acid; phosphorimidotriethioic acid; O-phenylphosphorimidothioic acid; O-benzylphosphorimidothioic acid; O-cyclohexylphosphorimidothioic acid; O-norbornylphosphorimidothioic acid; O,O'-diphenylphosphorimidothioic acid; O,O'-dibenzylphosphorimidothioic acid; O,O'-dicyclohexylphosphorimidothioic acid; and O,O'-dinorbornylphosphorimidothioic acid.

N-S Valence Stabilizer #6: Examples of phosphorothioic triamides, bis(phosphorothioic triamides), and poly(phosphorothioic triamides) (N-S Bidentates and N-S Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not

limited to: phosphorothioic triamide; phosphorothioic trihydrazide; phosphoramidothioic dihydrazide; N-phenylphosphorothioic triamide; N-benzylphosphorothioic triamide; N-cyclohexylphosphorothioic triamide; N-norbornylphosphorothioic triamide; N,N'-diphenylphosphorothioic triamide; N,N'-dibenzylphosphorothioic triamide; N,N'-dicyclohexylphosphorothioic triamide; and N,N'-dinorbornylphosphorothioic triamide.

5 N-S Valence Stabilizer #7: Examples of phosphoramidotriithioic acid, phosphorodiamidodithioic acid, bis(phosphoramidotriithioic acid), bis(phosphorodiamidodithioic acid),
10 poly(phosphoramidotriithioic acid), poly(phosphorodiamidodithioic acid), and derivatives thereof (N-S Bidentates and N-S Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: phosphoramidotriithioic acid, phosphorodiamidodithioic acid, S-phenylphosphoramidotriithioic acid, S-benzylphosphoramidotriithioic acid, S-cyclohexylphosphoramidotriithioic acid, S-norbornylphosphoramidotriithioic acid, S,S'-diphenylphosphoramidotriithioic acid, S,S'-dibenzylphosphoramidotriithioic acid, S,S'-dicyclohexylphosphoramidotriithioic acid, and S,S'-dinorbornylphosphoramidotriithioic acid.

15 N-S Valence Stabilizer #8: Examples of phosphoramidothioic acid, phosphoramidodithioic acid, phosphorodiamidothioic acid, bis(phosphoramidothioic acid), bis(phosphoramidodithioic acid),
20 bis(phosphorodiamidothioic acid), poly(phosphoramidothioic acid), poly(phosphoramidodithioic acid), and poly(phosphorodiamidothioic acid) (N-S Bidentates and N-S Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: phosphoramidothioic acid, phosphoramidodithioic acid, phosphorodiamidothioic acid, phosphorohydrazidothioic acid, phosphorohydrazidodithioic acid, phosphorodihydrazidothioic acid, phosphoramidothioic acid, O-phenylphosphoramidothioic acid, O-benzylphosphoramidothioic acid, O-cyclohexylphosphoramidothioic acid, O-norbornylphosphoramidothioic acid, S-phenylphosphoramidothioic acid, S-benzylphosphoramidothioic acid, S-cyclohexylphosphoramidothioic acid, and S-norbornylphosphoramidothioic acid.

N-S Valence Stabilizer #9: Examples of N-thioacyl 7-aminobenzylidenimines (N-S Bidentates or N-S Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: N-thioacetyl 7-methylaminobenzylidenimine; N-thioacetyl 7-phenylaminobenzylidenimine; N-thiobenzoyl 7-methylaminobenzylidenimine; and N-thiobenzoyl 7-phenylaminobenzylidenimine.

N-S Valence Stabilizer #10: Examples of thiohydroxamates (thiohydroxylamines), bis(thiohydroxamates), and poly(thiohydroxamates) (N-S Bidentates, N-S Tetridentates, and N-S Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: acetothiohydroxamic acid; propianothiohydroxamic acid; butyrothiohydroxamic acid; crotonothiohydroxamic acid; sorbothiohydroxamic acid; benzothiohydroxamic acid; toluidithiohydroxamic acid; salicylthiohydroxamic acid; phenylacetothiohydroxamic acid; anthranilthiohydroxamic acid; nicotinethiohydroxamic acid; picolinethiohydroxamic acid; cyclohexanethiohydroxamic acid; quinoline 8-thiohydroxamic acid; cinnamylthiohydroxamic acid; oxaldithiohydroxamic acid; succinylbis-N-phenylthiohydroxamic acid; adipylbis-N-phenylthiohydroxamic acid; glyoxalthiohydroxamic acid; 2-thiophenethiocarbohydroxamic acid; thenoylthiohydroxamic acid; N-phenylbenzothiohydroxamic acid; N-tolylbenzothiohydroxamic acid; N-phenylacetothiohydroxamic acid; N-phenyl-2-thenoylthiohydroxamic acid; and N-tolyl-2-thenoylthiohydroxamic acid.

N-S Valence Stabilizer #11: Examples of alpha- or ortho-aminothiocarboxylic acids, and alpha- or ortho-aminothiodicarboxylic acids, and derivatives thereof (N-S Bidentates, N-S Tridentates, and N-S Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-pyridinethiocarboxylic acid (thiopicolinic acid); 2-pyrazinethiocarboxylic acid; o-aminothiobenzoic acid; o-aminothionaphthoic acid; and 3,6-diaminothiophthalic acid.

N-S Valence Stabilizer #12: Examples of thiosemicarbazones, bis(thiosemicarbazones), and poly(thiosemicarbazones) (N-S Bidentates, N-S Tetridentates, and N-S Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited

to: acetaldehyde thiosemicarbazone; acetone thiosemicarbazone; pinacolone thiosemicarbazone; benzaldehyde thiosemicarbazone; naphthaldehyde thiosemicarbazone; norbornanone thiosemicarbazone; camphor thiosemicarbazone; nopinone thiosemicarbazone; 2-pyridinaldehyde thiosemicarbazone; salicylaldehyde thiosemicarbazone; quinolinaldehyde thiosemicarbazone; isatin dithiosemicarbazone; camphorquinone dithiosemicarbazone; camphorquinone dithiosemicarbazone; picolinaldehyde thiosemicarbazone; dipyridyl glyoxal dithiosemicarbazone; di-2-pyridyl ketone thiosemicarbazone; methyl-2-pyridyl ketone thiosemicarbazone; glyoxal dithiosemicarbazone; acetophenone thiosemicarbazone; biacetyl monoxime thiosemicarbazone; acetamido benzaldehyde thiosemicarbazone; 10 thymolaldothiosemicarbazone; thiophene-2-aldehyde thiosemicarbazone; phthalaldehyde dithiosemicarbazone; phthalimide dithiosemicarbazone; furaldehyde thiosemicarbazone; naphthoquinone thiosemicarbazone; phenanthrequinone thiosemicarbazone; cyclohexanedione dithiosemicarbazone; ionone thiosemicarbazone; bisthiosemicarbazone of diethyl-3,4-dioxadioate; pyridoxal alkylthiosemicarbazones; benzylidene phenylthiosemicarbazones; 15 lawsone thiosemicarbazone; and 1-benzoin-4-phenylthiosemicarbazone (bps).

N-S Valence Stabilizer #13: Examples of thioacyl hydrazones, bis(thioacyl hydrazones), and poly(thioacyl hydrazones) (N-S Bidentates, N-S Tetridentates, and N-S Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: acetaldehyde N-thioformylhydrazone; acetaldehyde N-thiobenzoylhydrazone; acetone N-thioformylhydrazone; acetone N-thiobenzoylhydrazone; pinacolone N-thioformylhydrazone; pinacolone N-thiobenzoylhydrazone; benzaldehyde N-thioformylhydrazone; benzaldehyde N-thiobenzoylhydrazone; naphthaldehyde N-thioformylhydrazone; naphthaldehyde N-thiobenzoylhydrazone; norbornanone N-thioformylhydrazone; norbornanone N-thiobenzoylhydrazone; camphor N-thioformylhydrazone; camphor N-thiobenzoylhydrazone; 25 nopinone N-thioformylhydrazone; nopinone N-thiobenzoylhydrazone; 2-pyridinaldehyde N-thioformylhydrazone; 2-pyridinaldehyde N-thiobenzoylhydrazone; salicylaldehyde N-thioformylhydrazone; salicylaldehyde N-thiobenzoylhydrazone; quinolinaldehyde N-thioformylhydrazone; quinolinaldehyde N-thiobenzoylhydrazone; thiophene-2-aldehyde N-thioformylhydrazone; thiophene-2-aldehyde N-thiobenzoylhydrazone; naphthoquinone N-thioformylhydrazone; naphthoquinone N-thiobenzoylhydrazone; ionone N-thioformylhydrazone;

ionone N-thiobenzoylhydrazone; benzaldehyde benzothiazolehydrazone; lawsone N-thioformylhydrazone; and lawsone N-thiobenzoylhydrazone.

5 N-S Valence Stabilizer #14: Examples of thiocarbazones (diazene carbothioic hydrazides), bis(thiocarbazones), and poly(thiocarbazones) (N-S Bidentates, N-S Tetridentates, and N-S Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diphenylthiocarbazone (dithizone); 2-phenylthiocarbazone; dinaphthylthiocarbazone; 2-naphthylthiocarbazone; and ambazone.

10 N-S Valence Stabilizer #15: Examples of azo compounds with thiol or mercapto or thiocarbonyl substitution at the ortho- (for aryl) or alpha- or beta- (for alkyl) positions, Bis[o-(HS-)] or alpha- or beta-(HS-)azo compounds], or Poly[o-(HS-)] or alpha- or beta-(HS-)azo compounds) (N-S Bidentates, N-S Tridentates, N-S Tetridentates, or N-S Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-thiolazobenzene [1-(phenylazo)-2-thiophenol]; 2,2'-dithioazobenzene; (2-thiophene)azobenzene; 1-(4-nitrophenylazo)-2-thionaphthol; 2-thiazolylazobenzene; and 2-benzothiazolylazobenzene.

20 N-S Valence Stabilizer #16: Examples of diazeneformothioamides, diazeneacetothioamides, bis(diazeneformothioamides), bis(diazeneacetothioamides), poly(diazeneformothioamides), and poly(diazeneacetothioamides) (N-S Bidentates, N-S Tetridentates, and N-S Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diazeneformothioamide, diazeneacetothioamide, phenyldiazeneformothioamide, diphenyldiazeneformothioamide, phenyldiazeneacetothioamide, and diphenyldiazeneacetothioamide.

25 N-S Valence Stabilizer #17: Examples of diazenecarbothioic acids, diazenecarbodithioic acids, bis(diazene carbothioic acids), bis(diazene carbodithioic acids), poly(diazene carbothioic acids), poly(diazene carbodithioic acids) and derivatives thereof (N-S Bidentates, N-S Tetridentates, N-S Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diazeneformothioic acid, diazeneacetothioic acid,

phenyldiazeneformothioic acid, diphenyldiazeneformothioic acid, phenyldiazeneacetothioic acid, and diphenyldiazeneacetothioic acid.

N-S Valence Stabilizer #18: Examples of diazeneformothioaldehydes,

5 diazeneacetothioaldehydes, bis(diazeneformothioaldehydes), bis(diazeneacetothioaldehydes), poly(diazeneformothioaldehydes), and poly(diazeneacetothioaldehydes) (N-S Bidentates, N-S Tetradentates and N-S Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diazeneformothioaldehyde, diazeneacetothioaldehyde, phenyldiazeneformothioaldehyde, phenyldiazeneacetothioaldehyde, and diphenyldiazeneacetothioaldehyde.

N-S Valence Stabilizer #19: Examples of diazenediformothioamides, diazenediacetothioamides, bis(diazenediformothioamides), bis(diazenediacetothioamides),

15 poly(diazenediformothioamides), and poly(diazenediacetothioamides) (N-S Tridentates and N-S Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diazenediformodithioamide, diazenediacetodithioamide, diphenyldiazenediformodithioamide, tetraphenyldiazenediformodithioamide, diphenyldiazenediacetodithioamide, and tetraphenyldiazenediacetodithioamide.

20 N-S Valence Stabilizer #20: Examples of diazenedicarbothioic acids, diazenedicarbodithioic acids, bis(diazenedicarbothioic acids), bis(diazenedicarbodithioic acids), poly(diazenedicarbothioic acids), poly(diazenedicarbodithioic acids) and derivatives thereof (N-S Tridentates and N-S Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diazenediformothioic acid, diazenediacetodithioic acid, phenyldiazenediformothioic acid, diphenyldiazenediformothioic acid, phenyldiazenediacetodithioic acid, and diphenyldiazenediacetodithioic acid.

N-S Valence Stabilizer #21: Examples of diazenediformothioaldehydes,

30 diazenediacetothioaldehydes, bis(diazenediformothioaldehydes), bis(diazenediacetothioaldehydes), poly(diazenediformothioaldehydes), and

poly(diazenediacetothioaldehydes) (N-S Tridentates and N-S Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diazenediformothioaldehyde, diazenediacetothioaldehyde, diphenyldiazenediformothioaldehyde, and diphenyldiazenediacetothioaldehyde.

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N-S Valence Stabilizer #22: Examples of ortho-thio (or -mercapto) substituted formazans, bis(o-thio or -mercapto substituted formazans), and poly(o-thio or -mercapto substituted formazans) (N-S Bidentates, N-S Tridentates, N-S Tetridentates, and N-S Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 1-(2-thiophenyl)-3,5-diphenylformazan; 1-(2-methylmercaptophenyl)-3,5-diphenylformazan; 1,5-bis(2-thiophenyl)-3-phenylformazan; and 5-bis(2-methylmercaptophenyl)-3-phenylformazan.

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N-S Valence Stabilizer #23: Examples of ortho-thio (or -mercapto) substituted azines (including ketazines), bis(o-thio or mercapto substituted azines), and poly(o-thio or mercapto substituted azines) (N-S Bidentates, N-S Tridentates, N-S Tetridentates, and N-S Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-mercato-1-benzalazine; 2-mercato-1-naphthalazine; and 2-mercato-1-cyclohexanonazine.

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N-S Valence Stabilizer #24: Examples of Schiff Bases with one Imine (C=N) Group and with ortho- or alpha- or beta-thio or mercapto or thiocarbonyl substitution (N-S Bidentates, N-S Tridentates, N-S Tetridentates, N-S Pentadentates, or N-S Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: N-(Thiosalicylaldehydo)isopropylamine; N-(2-thiophenecarboxaldehydo)isopropylamine; N-(2-Acetylthiopheno)isopropylamine; N-(2-Thioacetophenono)isopropylamine; N-(Thiosalicylaldehydo)cyclohexylamine; N-(2-Thiophenecarboxaldehydo)cyclohexylamine; N-(2-Acetylthiopheno)cyclohexylamine; N-(2-Thioacetophenono)cyclohexylamine; N-(Thiosalicylaldehydo)aniline; N-(2-Thiophenecarboxaldehydo)aniline; N-(2-Acetylthiopheno)aniline; N-(2-Thioacetophenono)aniline; N-(Thiosalicylaldehydo)aminonorbornane; N-(2-Thiocarboxaldehydo)aminonorbornane; N-(2-

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Acetylthiopheno)aminonorbornane; N-(2-Thioacetophenono)aminonorbornane; 4-aminobenzylidene-3-propyl-5-mercaptop-1,2,4-triazole; 4-aminocinnamalidene-3-propyl-5-mercaptop-1,2,4-triazole (acpm); 4-aminosalicylidene-3-propyl-5-mercaptop-1,2,4-triazole (aspmt); 4-aminovanillidene-3-propyl-5-mercaptop-1,2,4-triazole; 4-aminodimethylaminobenzylidene-3-propyl-5-mercaptop-1,2,4-triazole (adpm); cinnamylideneaminophenylthiazole; N-(2-mercaptophenyl)salicylideneimine; 2-thiophenecarboxaldehyde phenylhydrazone; 2-thiophenecarboxaldehyde 2-pyridyl hydrazone; 2-mercaptobenzaldehyde phenylhydrazone; and 2-mercaptobenzaldehyde 2-pyridyl hydrazone.
Also includes Schiff Bases derived from the reaction of carbonyl compounds with dithiocarbazates, and hydrazones with ortho-S substitution.

N-S Valence Stabilizer #25: Examples of Schiff Bases with two Imine (C=N) Groups and with ortho- or alpha- or beta-thio or mercapto or thiocarbonyl substitution (N-S Tridentates, N-S Tetradentates, N-S Pentadentates, or N-S Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: N,N’-(2,5-Thiophenedicarboxaldehydo)diisopropylamine; N,N’-(2,5-Thiophenedicarboxaldehydo)dicyclohexylamine; N,N’-(2,5-Thiophenedicarboxaldehydo)dianiline; N,N’-(2,5-Thiophenedicarboxaldehydo)di-aminonorbornane; N,N’-(o-Thiophthalicdialdehydo)diisopropylamine; N,N’-(o-Thiophthalicdialdehydo)dicyclohexylamine; N,N’-(o-Thiophthalicdialdehydo)dianiline; N,N’-(o-Thiophthalicdialdehydo)di-aminonorbornane; N,N’-(o-Thiophthalicdialdehydo)dicyclohexylamine; N,N’-(o-Thiophthalicdialdehydo)dianiline; N,N’-(o-Thioformylcamphoro)diisopropylamine; N,N’-(o-Thioformylcamphoro)dicyclohexylamine; N,N’-(o-Thioformylcamphoro)dianiline; N,N’-(o-Thioformylcamphoro)di-aminonorbornane; N,N’-(o-Thiodiacetylbenzeno)diisopropylamine; N,N’-(o-Thiodiacetylbenzeno)dicyclohexylamine; N,N’-(o-Thiodiacetylbenzeno)dianiline; N,N’-(3,6-Dithio-1,2-cyclohexanono)diisopropylamine; N,N’-(3,6-Dithio-1,2-cyclohexanono)dicyclohexylamine; N,N’-(3,6-Dithio-1,2-cyclohexanono)dianiline; N,N’-(3,6-Dithio-1,2-cyclohexanono)di-aminonorbornane; N,N’-(2,5-Diacetylthiopheno)diisopropylamine; N,N’-(2,5-Diacetylthiopheno)dicyclohexylamine; N,N’-(2,5-Diacetylthiopheno)dianiline; N,N’-(2,5-Diacetylthiopheno)di-aminonorbornane; N,N’-(Thiosalicylaldehydo)ethylenediamine; N,N’-(o-Thionaphthaldehydo)ethylenediamine; N,N’-(o-Thioacetophenono)ethylenediamine; ;

N,N'-(Thiosalicylaldehydo)trimethylenediamine; N,N'-(o-Thionaphthaldehydo)trimethylenediamine; N,N'-(o-Thioacetophenono)trimethylenediamine; ;
N,N'-(Thiosalicylaldehydo)cyclohexane-1,2-diamine; N,N'-(o-Thionaphthaldehydo)cyclohexane-1,2-diamine; N,N'-(o-Thioacetophenono)cyclohexane-1,2-diamine; N,N'-(Thiosalicylaldehydo)-1,2-diaminobenzene; N,N'-(o-Thionaphthaldehydo)-1,2-diaminobenzene; and N,N'-(o-Thioacetophenono)-1,2-diaminobenzene. Also includes Schiff Bases derived from the reaction of carbonyl compounds with dithiocarbazates, and hydrazones with ortho-S substitution.

10 N-S Valence Stabilizer #26: Examples of Schiff Bases with three Imine (C=N) Groups and with ortho- or alpha- or beta-thio or mercapto or thiocarbonyl substitution (N-S Tetridentates, N-S Pentadentates, or N-S Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: N,N',N''-(Thiosalicylaldehydo)tris(2-aminoethyl)amine; N,N',N''-(o-Thionaphthaldehydo)tris(2-aminoethyl)amine; and N,N',N''-(o-Thioacetophenono)tris(2-aminoethyl)amine. Also includes Schiff Bases derived from the reaction of carbonyl compounds with dithiocarbazates, and hydrazones with ortho-S substitution.

20 N-S Valence Stabilizer #27: Examples of thioalkyl amines (aminothiols or aminodisulfides) and thioalkyl imines (iminothiols or iminodisulfides) (N-S Bidentates, N-S Tridentates, N-S Tetridentates, and N-S Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-mercaptop-1-aminoethane; 2-methylmercapto-1-aminoethane; 3-mercaptop-1-aminopropane; 1-mercaptop-2-amino-2-methylpropane; 2-mercaptocyclohexylamine; 3-mercaptop-2-aminonorbornane; 1,3-dimercapto-2-aminopropane; 1,5-dimercapto-3-aminopentane; 2,2'-diaminodiethyl sulfide; 3,3'-diaminodipropyl sulfide; 2,2'-diaminodicyclohexyl sulfide; 1,6-dimercapto-3,4-diaminohexane; 1,7-dimercapto-3,5-diaminoheptane; 1,6-diamino-3,4-dimercaptohexane; 1,7-diamino-3,5-dimercaptoheptane; tri(mercaptomethyl)amine; tri(2-mercptoethyl)amine; dithiooxamide (rubeanic acid); 2,2'-diaminodiethyl disulfide; 3,3'-diaminodipropyl disulfide; 2,2'-diaminodicyclohexyl disulfide; 3-amino-1,5-pantanedithiodialdehyde; 3,4-diamino-1,6-hexanedithiodialdehyde; 3,5-diamino-1,7-heptanedithiodialdehyde; iminobisacetic acid; iminobispropionic acid; and bis(hydroxyethyl)aminoalkyl sulfide.

N-S Valence Stabilizer #28: Examples of thioaryl amines and thioaryl imines (N-S Bidentates, N-S Tridentates, N-S Tetridentates, and N-S Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-aminothiophenol (2-aminobenzene-thiol); 2-aminothiobenzoic acid (thioanthranilic acid); 2-aminothioanisole; 2-(methanamine)benzyl mercaptan [(2-aminomethyl)-alpha-toluenethiol] [(2-mercaptopethyl)-alpha-aminotoluene]; 1-amino-2-naphthalenethiol; 2-amino-1-naphthalenethiol; 2-amino-1-(methyl-disulfido)benzene; 2,2'-di(aminomethyl)diphenylthioketone; di(2-amino)phenyl sulfide; di(2-amino)phenyl disulfide (di-ortho-aminophenyl disulfide (doapd); 1,3-di(2-amino)phenyl-2-mercaptopropane; 1,3-di(3-amino)phenyl-2-mercaptopropane; 1,3-di(2-mercpto)phenyl-2-aminopropane; 1,3-di(3-mercpto)phenyl-2-aminopropane; 2,2'-dimercaptoiminodibenzyl; 2,2'-iminodibenzothioic acid; 2,2'-dimercaptoiminostilbene; and poly(o-aminothiophenol).

N-S Valence Stabilizer #29: Examples of five-membered heterocyclic rings containing one, two, three, or four nitrogen atoms at least one additional sulfur atom binding site not in a ring (N-S Bidentates, N-S Tridentates, N-S Tetridentates, or N-S Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-mercaptopyrrole; 2-(methylthio)methylpyrrole; 2,5-(thiomethyl)pyrrole; 2,5-(methylthiomethyl)pyrrole; 2,6-(methyl-disulfidomethyl)pyrrole; imidazoline-2-thione (2-mercaptopimidazole); 2-mercaptopthiazoline; 2-mercaptopbenzimidazole; 2-mercaptopbenzothiazole; 2-mercaptopbenzoxazole; 2-thiohydantoin; di-2-pyridylthioglyoxal (2,2'-thiopyridil); bis((1-pyrazolyl)methane)sulfide; bis((1-pyrazolyl)methane)disulfide; bis(2-(1-pyrazolyl)ethane)sulfide; bis(2-(1-pyrazolyl)ethane)disulfide; bis(benzimidazolylmethane)sulfide; bis(benzimidazolylethane)sulfide; bis(benzimidazolylmethane)disulfide; bis(benzimidazolylethane)disulfide; tris(imidazolyl)methanethiol; tris(imidazolylmethane)methanethiol; N-thiomethyl-N,N-(benzimidazolylmethane)amine; N-(2-thioethyl)-N,N-(benzimidazolylmethane)amine; N,N'-di(benzimidazolylmethane)-1,3-diamino-2-mercaptopropane; N,N,N',N'-tetrakis(benzimidazolylmethane)-1,3-diamino-2-mercaptopropane; bis(N,N-((4-imidazolyl)methane)2-aminoethane)sulfide; bis(N,N-((4-imidazolyl)methane)2-aminoethane)disulfide; 2-aminobenzothiazole (abt); 2-phenylaminothiazole; thiohydantoin; thioxohydropyrazole; 2-mercaptopbenzothiazole (mbt); 2-mercpto-1,3,4-thiadiazole; 2,5-

dimercapto-1,3,4-thiadiazole (bismuthiol); 2,5-bis(alkylthio)-1,3,4-thiadiazole; 2-amino-5-mercaptop-1,3,4-thiadiazole (amt); 5-mercaptotetrazole; 1-phenyl-5-mercaptotetrazole (pmt)(5-mptt); 5-mercaptotriazole; 3-mercaptotriazole; (2-benzothiazolyl)thioacetic acid; (2-benzothiazolyl)thiopropionic acid; (alkylthio)benzotriazoles; (arylthio)benzotriazoles; 2-mercaptopyrimidine; bis(5-mercaptop-1,2,4-triazol-3-yl); bis(5-mercaptop-1,2,4-triazol-3-yl)alkanes; 2-aminothiazolidine; thiazolidine-2-thione; 2-mercaptopthiazolidine; 1-(2-mercptoethyl)imidazoline; imidazolidine-2-thione; 4,5-dihydroxyimidazolidine-2-thione; 4-amino-5-mercaptop-1,2,4-triazole; (2-benzimidazolylthio)carboxylic acids; (2-benzoxazolylthio)carboxylic acids; (2-benzothiazolylthio)carboxylic acids; (2-benzimidazolylthio)hydroxyalkyl(aryl)s; (2-benzoxazolylthio)hydroxyalkyl(aryl)s; (2-benzothiazolylthio)hydroxyalkyl(aryl)s; 2-(phenylmethylthio)benzothiazole; 2,5-bis(hydrocarbyldithio)-1,3,4-thiadiazoles; 2-(hydrocarbyldithio)-5-mercaptop-1,3,4-thiadiazoles; bis(dithiobisthiadiazole); benzothiazolethione; 3-hydrazino-5-thio-1,2,4-triazole; imidazolidine-2,4-dithione; dimercaptobenzothiazole; 2-aminothiazole (atz); thiadiazole-2-thione; 5-mercaptopthiadiazole-2-thione; 1,1-thiocarbonyldiimidazole; phosphosphonomethylenethio-1,3-benzothiazole (pmbt); 4,5-dihydroxyimidazolidine-2-thione; imidazolidine-2-thione; 1,1'-thiocarbonyldiimidazole; 2,2'-dithiobis(benzothiazole); and 5,5'-dithiobis(tetrazole).

N-S Valence Stabilizer #30: Examples of six-membered heterocyclic rings containing one, two, three, or four nitrogen atoms at least one additional sulfur atom binding site not in a ring (N-S Bidentates, N-S Tridentates, N-S Tetridentates, or N-S Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 4-aminomethyl-3-pyridinemethanethiol (including thiopyridoxamine); 2-mercaptopyridine; 2-(methylthio)methylpyridine; 2-(2-(methylthio)ethyl)pyridine; 2,6-(thiomethyl)pyridine; 2,6-(methylthiomethyl)pyridine; 2,6-(methyldisulfidomethyl)pyridine; 2-mercaptopyrimidine; 2-dithiomethylpyrimidine; 2-mercaptoquinoline; 8-mercaptoquinoline (thioxine); 8-methylthioquinoline; 2-mercaptoquinazoline; thiorotic acid (1,2,3,6-tetrahydro-2,6-dithiono-4-pyrimidinecarboxylic acid) (6-thiouracilcarboxylic acid); 1-methylpyrimidine-2-thione; 2-thiouracil; 2,4-dithiouracil; 6-mercaptopurine; bis(N,N,N',N'-tetra(2-(2-pyridyl)ethane)aminomethane)sulfide; bis(N,N,N',N'-tetra(2-(2-pyridyl)ethane)aminomethane)disulfide; bis(N,N,N',N'-tetra(2-(2-

pyridyl)ethane)aminoethane)sulfide; bis(N,N,N',N'-tetra(2-(2-pyridyl)ethane)aminoethane)disulfide; 1,3,5-triazine-6-thione; 2-benzylmercapto-1,3,5-triazine; triazine dithiols [i.e., 6-(phenylamino)-1,3,5-triazine-2,4-dithiol (ptd); 6-aniline-1,3,5-triazine-2,4-dithiol (atd); and 2-(N,N-dialkylamino)-1,3,5-triazine-4,6-dithiol]; 2-thioquinazoline; 2-thioquinazolin-4-one; thiomorpholin-3-thione; [2-(aminomethyl)thio]pyridine; 6-mercaptopurine; dithiouracil; and 2,2'-dithiodipyridine (2,2'-dipyridyl disulfide).

- 5 N-S Valence Stabilizer #31: Examples of five-membered heterocyclic rings containing one or two sulfur atoms at least one additional nitrogen atom binding site not in a ring (N-S Bidentates, N-S Tridentates, N-S Tetridentates, or N-S Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-aminothiophene; 2,5-diaminothiophene; 2-aminomethylthiophene; 2,5-di(aminomethyl)thiophene; 2-aminobenzothiophene; and 2-iminothiolane.
- 10 N-S Valence Stabilizer #32: Examples of six-membered heterocyclic rings containing one or two sulfur atoms at least one additional nitrogen atom binding site not in a ring (N-S Bidentates, N-S Tridentates, N-S Tetridentates, or N-S Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-aminothiopyran; 2,6-diaminothiopyran; 2-aminomethylthiopyran; 2,6-di(aminomethyl)thiopyran; and 2-aminobenzothiopyran.
- 15 N-S Valence Stabilizer #33: Examples of five-membered heterocyclic rings containing one, two, three, or four nitrogen atoms at least one additional sulfur atom binding site in a separate ring (N-S Bidentates, N-S Tridentates, N-S Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-(2-thiophene)pyrrole; 2,5-di(2-thiophene)pyrrole; 2-(2-thiopyran)pyrrole; 2,5-di(2-thiopyran)pyrrole; 2,5-di(2-pyrrole)thiophene; 2,6-di(2-pyrrole)thiopyran; and 3,5-bis(2-thienyl)-4-amino-1,2,4-triazole (2-tat).
- 20 N-S Valence Stabilizer #34: Examples of six-membered heterocyclic rings containing one, two, three, or four nitrogen atoms at least one additional sulfur atom binding site in a separate ring (N-

S Bidentates, N-S Tridentates, N-S Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-(2-thiadiazolyl)benzimidazole; 2-(2-thiophene)pyridine; 2,6-di(2-thiophene)pyridine; 2-(2-thiopyran)pyridine; 2,6-di(2-thiopyran)pyridine; 2,5-di(2-pyridyl)thiophene; 2,6-di(2-pyridyl)thiopyran; and 2-(4-thiazolyl)benzimidazole.

N-S Valence Stabilizer #35: Examples of two-, three-, four-, six-, eight-, and ten-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of nitrogen (usually amine or imine groups) or sulfur (usually thiols, mercaptans, or thiocarbonyls) and are not contained in component heterocyclic rings (N-S Bidentates, N-S Tridentates, N-S Tetridentates, and N-S Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: azathiacyclobutane ([4]aneNS); azathiacyclopentane ([5]aneNS); azathiacyclohexane ([6]aneNS); azathiacycloheptane ([7]aneNS); azathiacyclooctane ([8]aneNS); azathiacyclobutene ([4]eneNS); azathiacyclopentene ([5]eneNS); azathiacyclohexene ([6]eneNS); azathiacycloheptene ([7]eneNS); azathiacyclooctene ([8]eneNS); azathiacyclobutadiene ([4]dieneNS); azathiacyclopentadiene ([5]dieneNS); azathiacyclohexadiene ([6]dieneNS); azathiacycloheptadiene ([7]dieneNS); azathiacyclooctadiene ([8]dieneNS); diazathiacyclohexane ([6]aneSN₂); diazathiacycloheptane ([7]aneSN₂); diazathiacyclooctane ([8]aneSN₂); diazathiacyclononane ([9]aneSN₂); diazathiacyclodecane ([10]aneSN₂); diazathiacycloundecane ([11]aneSN₂); diazathiacyclododecane ([12]aneSN₂); diazathiacyclohexene ([6]eneSN₂); diazathiacycloheptene ([7]eneSN₂); diazathiacyclooctene ([8]eneSN₂); diazathiacyclononene ([9]eneSN₂); diazathiacyclodecene ([10]eneSN₂); diazathiacycloundecene ([11]eneSN₂); diazathiacyclododecene ([12]eneSN₂); diazadithiacyclooctane ([8]aneS₂N₂); diazadithiacyclononane ([9]aneS₂N₂); diazadithiacyclodecane ([10]aneS₂N₂); diazadithiacycloundecane ([11]aneS₂N₂); diazadithiacyclododecane ([12]aneS₂N₂); diazadithiacyclotridecane ([13]aneS₂N₂); diazadithiacyclotetradecane ([14]aneS₂N₂); diazadithiacyclopentadecane ([15]aneS₂N₂); diazadithiacyclohexadecane ([16]aneS₂N₂); diazadithiacycloheptadecane ([17]aneS₂N₂); diazadithiacyclooctadecane ([18]aneS₂N₂); diazadithiacyclononadecane ([19]aneS₂N₂); diazadithiacycloeicosane ([20]aneS₂N₂);

diazadithiacyclooctadiene ([8]dieneS₂N₂); diazadithiacyclononadiene ([9]dieneS₂N₂); diazadithiacyclodecadiene ([10]dieneS₂N₂); diazadithiacycloundecadiene ([11]dieneS₂N₂); diazadithiacyclododecadiene ([12]dieneS₂N₂); diazadithiacyclotridecadiene ([13]dieneS₂N₂); diazadithiacyclotetradecadiene ([14]dieneS₂N₂); diazadithiacyclopentadecadiene ([15]dieneS₂N₂); diazadithiacyclohexadecadiene ([16]dieneS₂N₂); diazadithiacycloheptadecadiene ([17]dieneS₂N₂); diazadithiacyclooctadecadiene ([18]dieneS₂N₂); diazadithiacyclononadecadiene ([19]dieneS₂N₂); diazadithiacycloicosadiene ([20]dieneS₂N₂); and tetramethyldithiahexaaazacyclobidecanehexaene (mtab).

10 N-S Valence Stabilizer #36: Examples of four-, six-, eight-, or ten-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes and sepulchrates) wherein all binding sites are composed of nitrogen or sulfur and are contained in component heterocyclic rings (N-S Bidentates, N-S Tridentates, N-S Tetridentates, or N-S Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dithiopyrandipyridines; dithiophenedipyrroles; trithiopyrantripyridines; trithiophenetripyrroles; tetrathiopyrantetrapyridines; and tetrathiophenetetrapyrrroles.

20 N-S Valence Stabilizer #37: Examples of four-, six-, eight-, or ten-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of nitrogen or sulfur and are contained in a combination of heterocyclic rings and amine, imine, thiol, mercapto, or thiocabonyl groups (N-S Bidentates, N-S Tridentates, N-S Tetridentates, or N-S Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: azathiatetraphyrins; diazadithiatetraphyrins; azathiahexaphyrins; diazadithiahexaphyrins; and triazatrithiahexaphyrins.

30 N-O Valence Stabilizer #1: Examples of N-hydroxy(or N,N'-dihydroxy)amidines and N-hydroxy(or N,N'-dihydroxy)diamidines (N-O bidentates, N-O tridentates, or N-O tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: N-hydroxy-N,N'-dimethylformamidine; N-hydroxy-N,N'-diethylformamidine; N-

hydroxy-N,N'-diisopropylformamidine; N-hydroxy-N,N'-dibutylformamidine; N-hydroxy-N,N'-
5 diphenylformamidine; N-hydroxy-N,N'-dibenzylformamidine; N-hydroxy-N,N'-
dinaphthylformamidine; N-hydroxy-N,N'-dicyclohexylformamidine; N-hydroxy-N,N'-
dinorbornylformamidine; N-hydroxy-N,N'-diadamantylformamidine; N-hydroxy-N,N'-
dianthraquinonylformamidine; N-hydroxy-N,N'-dimethylacetamide; N-hydroxy-N,N'-
10 diethylacetamide; N-hydroxy-N,N'-diisopropylacetamide; N-hydroxy-N,N'-
dibutylacetamide; N-hydroxy-N,N'-diphenylacetamide; N-hydroxy-N,N'-
dibenzylacetamide; N-hydroxy-N,N'-dinaphthylacetamide; N-hydroxy-N,N'-
dicyclohexylacetamide; N-hydroxy-N,N'-dinorbornylacetamide; N-hydroxy-N,N'-
15 diadamantylacetamide; N-hydroxy-N,N'-dimethylbenzamide; N-hydroxy-N,N'-
diethylbenzamide; N-hydroxy-N,N'-diisopropylbenzamide; N-hydroxy-N,N'-
dibutylbenzamide; N-hydroxy-N,N'-diphenylbenzamide; N-hydroxy-N,N'-
dibenzylbenzamide; N-hydroxy-N,N'-dinaphthylbenzamide; N-hydroxy-N,N'-
20 dicyclohexylbenzamide; N-hydroxy-N,N'-dinorbornylbenzamide; N-hydroxy-N,N'-
diadamantylbenzamide; N-hydroxy-N,N'-dimethyltoluamide; N-hydroxy-N,N'-
diethyltoluamide; N-hydroxy-N,N'-diisopropyltoluamide; N-hydroxy-N,N'-
dibutyltoluamide; N-hydroxy-N,N'-diphenyltoluamide; N-hydroxy-N,N'-
dibenzyltoluamide; N-hydroxy-N,N'-dinaphthyltoluamide; N-hydroxy-N,N'-
25 dicyclohexyltoluamide; N-hydroxy-N,N'-dinorbornyltoluamide; N-hydroxy-N,N'-
diadamantyltoluamide; N,N-dihydroxyoxalic diamidine; N,N'-dihydroxymalonic diamidine;
N,N'-dihydroxysuccinic diamidine; N,N'-dihydroxyglutaric diamidine; N,N'-dihydroxyadipic
diamidine; N,N'-dihydroxypimelic diamidine; N,N'-dihydroxysuberic diamidine; N,N'-
dihydroxyphthalic diamidine; N,N'-dihydroxyterephthalic diamidine; N,N'-dihydroxyisophthalic
diamidine; N,N'-dihydroxypiperazine diamidine.

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N-O Valence Stabilizer #2: Examples of guanylureas, guanidinoureas, bis(guanylureas),
bis(guanidinoureas), poly(guanylureas), and poly(guanidinoureas) (N-O Bidentates and N-O
Tetradentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴
30 include, but are not limited to: guanylurea (amidinourea)(dicyandiamidine); guanidinourea;
methylguanylurea; ethylguanylurea; isopropylguanylurea; butylguanylurea; benzylguanylurea;
phenylguanylurea; tolylguanylurea; naphthylguanylurea; cyclohexylguanylurea;

norbornylguanylurea; adamantylguanylurea; dimethylguanylurea; diethylguanylurea; diisopropylguanylurea; dibutylguanylurea; dibenzylguanylurea; diphenylguanylurea; ditolylguanylurea; dinaphthylguanylurea; dicycbhexylguanylurea; dinorbornylguanylurea; diadamantylguanylurea; ethylenebis(guanylurea); propylenebis(guanylurea);
5 phenylenebis(guanylurea); piperazinebis(guanylurea); oxalylbis(guanylurea); malonylbis(guanylurea); succinylbis(guanylurea); phthalylbis(guanylurea); 2-ureidothiazole; 2-ureidooxazole; 2-ureidoimidazole; 3-ureidopyrazole; 3-ureido-1,2,4-triazole; and 5-ureidotetrazole.

10 N-O Valence Stabilizer #3: Examples of amidinoamides, guanidinoamides, bis(amidinoamides), bis(guanidinoamides), poly(amidinoamides), and poly(guanidinoamides) (including both N-amidinoamides and 2-amidinoacetamides) (N-O Bidentates, N-O Tridentates, and N-O Tetradentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: amidinoacetamide (1-acetylguanidine); guanidinoacetamide;
15 amidinopropanamide; amidinobutanamide; amidinobenzamide; amidinotoluamide; amidinocyclohexamide; N-methylamidinoacetamide; N-ethylamidinopropanamide; N-propylamidinobutanamide; N-phenylamidinobenzamide; N-tolylamidinotoluamide; N-cyclohexylamidinocyclohexamide; bis(amidinoxamide); bis(amidinomalonamide); bis(amidinosuccinamide); bis(amidinophthalamide); 2-amidinoacetamide (malonamidine); N-
20 methyl-2-amidinoacetamide; N-ethyl-2-amidinoacetamide; N-phenyl-2-amidinoacetamide; N-benzyl-2-amidinoacetamide; N-cyclohexyl-2-amidinoacetamide; N,N'-dimethyl-2-amidinoacetamide; N,N'-diethyl-2-amidinoacetamide; N,N'-diphenyl-2-amidinoacetamide; N,N'-dibenzyl-2-amidinoacetamide; N,N'-dicyclohexyl-2-amidinoacetamide; 2-N-acylaminothiazole; 2-N-acylaminooxazole; 2-N-acylaminimidazole; 3-N-acylaminopyrazole; 3-N-acylamo-1,2,4-triazole; and 5-N-acylaminotetrazole.
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30 N-O Valence Stabilizer #4: Examples of imidoylamides, bis(imidoylamides), and poly(imidoylamides) (N-O Bidentates, N-O Tridentates, and N-O Tetradentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to:
acetimidoylacetamide; acetimidoylpropanamide; acetimidoylbutanamide; acetimidoylbenzamide; acetimidolytoluamide; acetimidoylcyclohexamide;

propimidoylpropanamide; butimidoylbutanamide; benzimidoylbenzamide; ethylenebis(acetimidoylacetamide); propylenebis(acetimidoylacetamide); and phenylenebis(acetimidoylacetamide).

- 5 N-O Valence Stabilizer #5: Examples of O-amidinocarbamates, bis(O-amidinocarbamates), and poly(O-amidinocarbamates) (N-O Bidentates and N-O Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: O-amidinocarbamate; N-methyl-O-amidinocarbamate; N-ethyl-O-amidinocarbamate; N-isopropyl-O-amidinocarbamate; N-butyl-O-amidinocarbamate; N-benzyl-O-amidinocarbamate; N-phenyl-O-amidinocarbamate; N-tolyl-O-amidinocarbamate; N-naphthyl-O-amidinocarbamate; N-cyclohexyl-O-amidinocarbamate; N-norbornyl-O-amidinocarbamate; N-adamantyl-O-amidinocarbamate; N,N'-dimethyl-O-amidinocarbamate; N,N'-diethyl-O-amidinocarbamate; N,N'-diisopropyl-O-amidinocarbamate; N,N'-dibutyl-O-amidinocarbamate; N,N'-dibenzyl-O-amidinocarbamate; N,N'-diphenyl-O-amidinocarbamate; N,N'-ditolyl-O-amidinocarbamate; N,N'-dinaphthyl-O-amidinocarbamate; N,N'-dicyclohexyl-O-amidinocarbamate; N,N'-dinorbornyl-O-amidinocarbamate; N,N'-diadamantyl-O-amidinocarbamate; ethylenebis(O-amidinocarbamate); propylenebis(O-amidinocarbamate); phenylenebis(O-amidinocarbamate); piperazinebis(O-amidinocarbamate); oxalylbis(O-amidinocarbamate); malonylbis(O-amidinocarbamate); succinylbis(O-amidinocarbamate); phthalylbis(O-amidinocarbamate); 2-O-carbamatothiazole; 2-O-carbamatooxazole; 2-O-carbamatoimidazole; 3-O-carbamatopyrazole; 3-O-carbamato-1,2,4-triazole; and 5-carbamatotetrazole.
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- 25 N-O Valence Stabilizer #6: Examples of S-amidinothiocarbamates, bis(S-amidinothiocarbamates), and poly(S-amidinothiocarbamates) (N-O Bidentates and N-O Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: S-amidinothiocarbamate; N-methyl-S-amidinothiocarbamate; N-ethyl-S-amidinothiocarbamate; N-isopropyl-S-amidinothiocarbamate; N-butyl-S-amidinothiocarbamate; N-benzyl-S-amidinothiocarbamate; N-phenyl-S-amidinothiocarbamate; N-tolyl-S-amidinothiocarbamate; N-naphthyl-S-amidinothiocarbamate; N-cyclohexyl-S-amidinothiocarbamate; N-norbornyl-S-amidinothiocarbamate; N-adamantyl-S-amidinothiocarbamate; N,N'-dimethyl-S-amidinothiocarbamate; N,N'-diethyl-S-
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amidinothiocarbamate; N,N'-diisopropyl-S-amidinothiocarbamate; N,N'-dibutyl-S-amidinothiocarbamate; N,N'-dibenzyl-S-amidinothiocarbamate; N,N'-diphenyl-S-amidinothiocarbamate; N,N'-ditolyl-S-amidinothiocarbamate; N,N'-dinaphthyl-S-amidinothiocarbamate; N,N'-dicyclohexyl-S-amidinothiocarbamate; N,N'-dinorbornyl-S-amidinothiocarbamate; N,N'-diadamantyl-S-amidinothiocarbamate; ethylenebis(S-amidinothiocarbamate); propylenebis(S-amidinothiocarbamate); phenylenebis(S-amidinothiocarbamate); piperazinebis(S-amidinothiocarbamate); oxalylbis(S-amidinothiocarbamate); malonylbis(S-amidinothiocarbamate); succinylbis(S-amidinothiocarbamate); phthalylbis(S-amidinothiocarbamate); 2-O-monothiocarbamatothiazole; 2-O-monothiocarbamatooxazole; 2-O-monothiocarbamatoimidazole; 3-O-monothiocarbamatopyrazole; 3-O-monothiocarbamato-1,2,4-triazole; and 5-O-monothiocarbamatotetrazole.

N-O Valence Stabilizer #7: Examples of diimidosulfuric acid, bis(diimidosulfuric acid), and derivatives thereof (N-O Bidentates and N-O Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diimidosulfuric acid; O-phenyldiimidosulfuric acid; O-benzylidiimidosulfuric acid, O-cyclohexyldiimidosulfuric acid, O-norbornyldiimidosulfuric acid, O,O'-diphenyldiimidosulfuric acid; O,O'-dibenzylidiimidosulfuric acid, O,O'-dicyclohexyldiimidosulfuric acid, and O,O'-dinorbornyldiimidosulfuric acid.

N-O Valence Stabilizer #8: Examples of phosphorimidic acid, bis(phosphorimidic acid); and poly(phosphorimidic acid), and derivatives thereof (N-O Bidentates, N-O Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: phosphorimidic acid; O-phenylphosphorimidic acid; O-benzylphosphorimidic acid; O-cyclohexylphosphorimidic acid; O-norbornylphosphorimidic acid; O,O'-diphenylphosphorimidic acid; O,O'-dibenzylphosphorimidic acid; O,O'-dicyclohexylphosphorimidic acid; and O,O'-dinorbornylphosphorimidic acid.

N-O Valence Stabilizer #9: Examples of phosphoric triamides, bis(phosphoric triamides), and poly(phosphoric triamides) (N-O Bidentates and N-O Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: phosphoric

triamide; phosphoramidic dihydrazide; N-phenylphosphoric triamide, N-benzylphosphoric triamide; N-cyclohexylphosphoric triamide; N-norbornylphosphoric triamide; N,N'-diphenylphosphoric triamide, N,N'-dibenzylphosphoric triamide; N,N'-dicyclohexylphosphoric triamide; and N,N'-dinorbornylphosphoric triamide.

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N-O Valence Stabilizer #10: Examples of phosphoramidic acid, phosphorodiamidic acid, bis(phosphoramidic acid), bis(phosphorodiamidic acid), poly(phosphoramidic acid), poly(phosphorodiamidic acid), and derivatives thereof (N-O Bidentates and N-O Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: phosphoramidic acid, phosphorodiamidic acid, phosphoramidohydrazidic acid; phosphorohydrazidic acid; phosphorodihydrazidic acid; O-phenylphosphoramidic acid; O-benzylphosphoramidic acid; O-cyclohexylphosphoramidic acid; O-norbornylphosphoramidic acid; O,O'-diphenylphosphoramidic acid; O,O'-dibenzylphosphoramidic acid; O,O'-dicyclohexylphosphoramidic acid; and O,O'-dinorbornylphosphoramidic acid.

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N-O Valence Stabilizer #11: Examples of N-acyl 7-aminobenzylidenimines (N-O Bidentates or N-O Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: N-acetyl 7-methylaminobenzylidenimine; N-acetyl 7-phenylaminobenzylidenimine; N-benzoyl 7-methylaminobenzylidenimine; and N-benzoyl 7-phenylaminobenzylidenimine.

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N-O Valence Stabilizer #12: Examples of oximes, dioximes, and poly(oximes) (N-O Bidentates, N-O Tridentates, and N-O Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: acetaldoxime (Hado); acetoxime (acetone oxime)(Hato); butanone oxime; pentanone oxime; hexanone oxime; pinacolone oxime; heptanone oxime; octanone oxime; cyclopentanone oxime; cyclohexanone oxime; cycloheptanone oxime; cyclooctanone oxime; cyclopentanedione dioxime; cyclohexanedione dioxime; cycloheptanedione dioxime; cyclooctanedione dioxime; isatin dioxime; benzaldehyde oxime; naphthaldehyde oxime; norbornanone oxime; camphor oxime; dimethylglyoxime (H₂DMG); diethylglyoxime; diisopropylglyoxime; diterbutylglyoxime; dicyanoglyoxime; dicyanamidoglyoxime; diphenylglyoxime (Hdfg); dibenzylglyoxime; dicyclohexylglyoxime;

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dinorbornylglyoxime; camphorquinone dioxime (Hcqd); nopinoquinone dioxime (Hnqd); butyraldoxime; propionaldoxime; furildioxime; and thienyldioxime.

N-O Valence Stabilizer #13: Examples of carbonyl oximes, bis(carbonyl oximes), and poly(carbonyl oximes) (N-O Bidentates, N-O Tridentates, and N-O Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diacetyl monoxime (2,3-butanedione monoxime); benzil monoxime (1,2-diphenylethanedione monoxime); 1,2-dicyclohexylethanedione monoxime; 1,2-(trifluoromethyl)ethanedione monoxime; 1,2-dinorbornylethanedione monoxime; cyclopentanedione monoxime; cyclohexanedione monoxime; cycloheptanedione monoxime; cyclooctanedione monoxime; camphorquinone oxime; 3-hydroxyiminopentane-2,4-dione; and 4-isonitrosopyralozone.

N-O Valence Stabilizer #14: Examples of imine oximes, bis(imine oximes), and poly(imine oximes) (including 2-nitrogen heterocyclic oximes) (N-O Bidentates, N-O Tridentates, N-O Tetridentates, and N-O Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 3-(methylimino)butan-2-one oxime; 4-(methylimino)hexan-3-one oxime; 1,2-diphenyl-2-(methylimino)ethan-1-one oxime; 1,2-diphenyl-2-(phenylimino)ethan-1-one oxime; 1,2-dicyclohexyl-2-(methylimino)ethan-1-one oxime; 1,2-dicyclohexyl-2-(cyclohexylimino)ethan-1-one oxime; 1,2-dinorbornyl-2-(methylimino)ethan-1-one oxime; N,N'-methylenebis-(3-iminobutan-2-one oxime); N,N'-methylenebis-(4-iminohexan-3-one oxime); N,N'-methylenebis-(1,2-diphenyl-2-iminoethan-1-one oxime); N,N'-methylenebis-(1,2-dicyclohexyl-2-iminoethan-1-one oxime); N,N'-methylenebis-(1,2-dinorbornyl-2-iminoethan-1-one oxime); N,N'-ethylenebis-(3-iminobutan-2-one oxime); N,N'-ethylenebis-(4-iminohexan-3-one oxime); N,N'-ethylenebis-(1,2-diphenyl-2-iminoethan-1-one oxime); N,N'-ethylenebis-(1,2-dicyclohexyl-2-iminoethan-1-one oxime); N,N'-ethylenebis-(1,2-dinorbornyl-2-iminoethan-1-one oxime); N,N'-propylenebis-(3-iminobutan-2-one oxime); N,N'-propylenebis-(4-iminohexan-3-one oxime); N,N'-propylenebis-(1,2-diphenyl-2-iminoethan-1-one oxime); N,N'-propylenebis-(1,2-dicyclohexyl-2-iminoethan-1-one oxime); N,N'-propylenebis-(1,2-dinorbornyl-2-iminoethan-1-one oxime); diacetylazine oxime (Hazio); 2-pyridinaldoxime (Hpao); methyl 2-pyridyl ketone oxime; ethyl 2-pyridyl ketoxime; phenyl 2-pyridyl ketone oxime (Hppk); benzyl 2-pyridyl ketoxime; di(2-pyridyl)

ketone oxime; methyl 2-pyrrolyl ketone oxime; ethyl 2-pyrrolyl ketone oxime; phenyl 2-pyrrolyl ketone oxime; di(2-pyrrolyl) ketone oxime; and tris(2-aldoximo-6-pyridyl)phosphine.

N-O Valence Stabilizer #15: Examples of hydroxy oximes, bis(hydroxy oximes), and poly(hydroxy oximes) (including 2-oxygen heterocyclic oximes) (N-O Bidentates, N-O Tridentates, N-O Tetridentates, and N-O Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 3-hydroxybutan-2-one oxime; 4-hydroxyhexan-3-one oxime; benzoin oxime (bo)(1,2-diphenyl-2-hydroxyethanone oxime); 1,2-di(trifluoromethyl)-2-hydroxyethanone oxime; 1,2-dicyclohexyl-2-hydroxyethanone oxime; 1,2-dinorbornyl-2-hydroxyethanone oxime; salicylaldoxime (so)(saldox); 2-hydroxy-1-naphthaldehyde oxime; 2-furanaldoxime; furildioxime; methyl 2-furanyl ketone oxime; ethyl 2-furanyl ketoxime; phenyl 2-furanyl ketone oxime; benzyl 2-furanyl ketoxime; di(2-furanyl) ketone oxime; and 2,5-(oximinomethyl)phenol.

N-O Valence Stabilizer #16: Examples of amino oximes, bis(amino oximes), and poly(amino oximes) (N-O Bidentates, N-O Tridentates, N-O Tetridentates, and N-O Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 3-(methylamino)butan-2-one oxime (HMeabo); 4-(methylamino)hexan-3-one oxime (HEtabo); 1,2-diphenyl-2-(methylamino)ethanone oxime (HPhabo); 1,2-diphenyl-2-(phenylamino)ethanone oxime; 1,2-dicyclohexyl-2-(methylamino)ethanone oxime (HcyHxabo); 1,2-dicyclohexyl-2-(cyclohexylamino)ethanone oxime; 1,2-di(trifluoromethyl)-2-(methylamino)ethanone oxime; 1,2-dinorbornyl-2-(methylamino)ethanone oxime (HNorbabo); N,N'-ethylenebis-(3-aminobutan-2-one oxime)(Haboen); N,N'-ethylenebis-(4-amino hexan-3-one oxime); N,N'-ethylenebis-(1,2-diphenyl-2-aminoethanone oxime); N,N'-ethylenebis-(1,2-dicyclohexyl-2-aminoethanone oxime); N,N'-ethylenebis-(1,2-di(trifluoromethyl)-2-aminoethanone oxime); N,N'-ethylenebis-(1,2-dinorbornyl-2-aminoethanone oxime); N,N'-propylenebis-(3-aminobutan-2-one oxime)(Habopn); N,N'-propylenebis-(4-amino hexan-3-one oxime); N,N'-propylenebis-(1,2-diphenyl-2-aminoethanone oxime); N,N'-propylenebis-(1,2-dicyclohexyl-2-aminoethanone oxime); N,N'-propylenebis-(1,2-di(trifluoromethyl)-2-aminoethanone oxime); N,N'-propylenebis-(1,2-dinorbornyl-2-aminoethanone oxime); 2,2'-iminobis(acetamidoxime); 1-diethylamino-3-butanoloxime; and di-2-pyridyl ketone oxime.

N-O Valence Stabilizer #17: Examples of amido oximes, bis(amido oximes), and poly(amido oximes) (N-O Bidentates, N-O Tridentates, N-O Tetridentates, and N-O Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: formamide oxime; acetamide oxime; propanamide oxime; butanamide oxime; benzamide oxime (Hbamox); naphthamide oxime; diformamide dioxime; salicylamide oxime; and 4-imidazolamide oxime.

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N-O Valence Stabilizer #18: Examples of azo oximes, bis(azo oximes), and poly(azo oximes) (N-O Bidentates, N-O Tridentates, N-O Tetridentates, and N-O Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: acetaldehyde phenylhydrazone oxime; propionaldehyde phenylhydrazone oxime; and benzaldehyde phenylhydrazone oxime. Also includes hydrazone oximes.

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N-O Valence Stabilizer #19: Examples of 2-nitrosophenols (o-quinone monoximes) (N-O Bidentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-nitrosophenol; 1-nitroso-2-naphthol (Honn); 2-nitroso-1-naphthol (Htnn); 3-nitrosopyrocatechol; 3,6-dinitrosopyrocatechol; 2-nitrosoresorcinol; 2,4-dinitrosoresorcinol; 2,4,6-trinitrosoresorcinol; 2-nitrosohydroquinone; 2,6-dinitrosohydroquinone; 2,3,5,6-tetranitrosohydroquinone; 4-nitrosopyrogallol; 4,6-dinitrosopyrogallol; 2-nitrosophloroglucinol; 2,4,6-trinitrosophloroglucinol; 7-nitroso-6-hydroxyindazole; Pigment Green 12 (C.I. 10020); Naphthol Green; and nitroso-R-salt.

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N-O Valence Stabilizer #20: Examples of 2-nitrophenols (N-O Bidentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-nitrophenol; 2,3-dinitrophenol; 2,4-dinitrophenol; 2,5-dinitrophenol; 2,6-dinitrophenol; 2,4,6-trinitrophenol (picric acid); 2-amino-4,6-dinitrophenol (picramic acid); 1-nitro-2-naphthol; 2-nitro-1-naphthol; 3-nitropyrocatechol; 3,6-dinitropyrocatechol; 2-nitrosoresorcinol; 2,4-dinitrosoresorcinol; 2,4,6-trinitrosoresorcinol (styphnic acid); 2-nitrosohydroquinone; 2,6-dinitrosohydroquinone; 2,3,5,6-tetranitrosohydroquinone; 4-nitropyrogallol; 4,6-dinitropyrogallol; 2-nitrophloroglucinol; 2,4,6-trinitrophloroglucinol; dinitrocresol; 7-nitro-6-hydroxyindazole; Dinoseb; Eosin; Naphthol Yellow; and Martius Yellow.

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N-O Valence Stabilizer #21: Examples of hydroxamates (hydroxylamines), bis(hydroxamates), and poly(hydroxamates) (N-O Bidentates, N-O Tetridentates, and N-O Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: acetohydroxamic acid; propianohydroxamic acid; butyrohydroxamic acid;

- 5 crotonohydroxamic acid; sorbohydroxamic acid; benzohydroxamic acid (BH₂); toluichydroxamic acid; salicylhydroxamic acid (SH₂); phenylacetohydroxamic acid (PhH₂); anthranilhydroxamic acid (AnH₂); nicotinehydroxamic acid (NicH₂); picolinehydroxamic acid; cyclohexanehydroxamic acid (CH₂); quinoline 8-hydroxamic acid (QH₂); cinnamylhydroxamic acid (CnH₂); oxaldihydroxamic acid (OxalH₂); succinylbis-N-phenylhydroxamic acid (SuH₂); adipylbis-N-phenylhydroxamic acid (AdH₂); glyoxalhydroxamic acid (GH₂); 2-thiophenecarbohydroxamic acid; thenoylhydroxamic acid; N-phenylbenzohydroxamic acid; N-tolylbenzohydroxamic acid; N-phenylacetohydroxamic acid; N-phenyl-2-thenoylhydroxamic acid; N-tolyl-2-thenoylhydroxamic acid; and polyhydroxamic acids.

- 10 15 N-O Valence Stabilizer #22: Examples of N-nitrosohydroxylamines, bis(N-nitrosohydroxylamines), and poly(N-nitrosohydroxylamines) (N-O Bidentates, N-O Tetridentates, and N-O Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: N-nitrosophenylhydroxylamine (cupferron); N-nitrosonaphthylhydroxylamine (neocupferron); N-nitrosoanthracylhydroxylamine; N-nitroso(2-pyridyl)hydroxylamine; and N-nitroso(2-thiophenyl)hydroxylamine.

- 20 25 N-O Valence Stabilizer #23: Examples of amino acids, ortho-aminocarboxylic acids, peptides, polypeptides, and proteins [N-O Bidentates, N-O Tridentates, and N-O Tetridentates; possibly S-O dentates for sulfur-contg. examples such as penicillamine and cystine] that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: alanine (Ala); arginine (Arg); asparagine (Asn); aspartic acid (Asp); cysteine (Cys); cystine (Cys or Cys.Cys); dihydroxyphenylalanine (Dopa); glutamic acid (Glu); glutamine (Gln); glycine (Gly); histidine (His); isoleucine (Ile); leucine (Leu); lysine (Lys); methionine (Met); penicillamine (Pen); phenylalanine (Phe); tolylalanine (tala); proline (Pro); sarcosine; serine (Ser); threonine (Thr); tryptophan (Trp); tyrosine (Tyr); and valine (Val) as amino acid examples; 2-pyridinecarboxylic acid (picolinic acid), 2-pyrazinecarboxylic acid, 2,3-

dicarboxypyrazine, and anthranilic acid as ortho-aminocarboxylic acid examples; Gly-GluO; Hgly-Gly; Gly-MetO; Met-GlyO; Gly-TyrO; Ala-HisO; Gly-His-GlyO; Gly-Gly-His; Gly-Leu-TyrO; penta-GlyO; His-His; triaminoisobutyrate; tetra-GlyO; Pro-Gly; and Gly-Met as peptide examples; and azurin, carbonic anhydrase C; carboxypeptidase; concanavalin A; cytochrome b; cytochrome c; erythrocrorulin; ferredoxin; haemerythrin; haemoglobin; myoglobin; parvalbumin; albumin; plastocyanin; rubredoxin; superoxide dismutase; thermolysin; and trypsin as protein examples; N-acylamino acids; aminocaproic acid; and 3,5-diiodotyrosine.

N-O Valence Stabilizer #24: Examples of amides, bis(amides), and poly(amides), including lactams (N-O bidentates, N-O tridentates, and N-O tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: acetamide; propionamide; butanamide; benzamide (benzoylamine)(1-phenylformamide); 1-naphthylformamide; toluamide; 1-cyclohexylformamide; 1-norbornylformamide; 1-adamantylformamide; N,N-dimethylformamide (DMF)(DMFA); N,N-dimethylacetamide (DMAC); N,N-dimethylbenzamide; N,N-diethylformamide; N,N-diethylacetamide; decanamide; dodecanamide; tetradecanamide; hexadecanamide; octadecanamide; lactobionic acid amide; (hydroxyalkylthio)succinamides; (mercaptoalkoxy)succinamides; polycaproamides; glycinamide; aminoalkylanilides; amidopolyamines (apa); bis(1-phenylethylamide); oxalic semiamide; malonic semiamide; succinic semiamide; bis(1,1'-benzotriazolyl)dicarboxamide; nicotinamide; acetanilide (N-phenylacetamide); formanilide (N-phenylformamide); benzanilide (N-phenylbenzamide); N-methylformanilide; acetanilide; nicotinanilide; 4'-hydroxyacetanilide (acetaminophen); 2-pyrrolidone; methyl-2-pyrrolidone (NMP); 2-piperidone (valerolactam); caprolactam; polymethylenepolyamine dipropionamide; polyacrylamides; polypyrrolidones [including polyvinylpyrrolidone (povidone)(PVP)]; pyrazolidinones; pyrazolones; diazepinones; N-alkylazaalkene lactams; and N-(2-hydroxyalkyl)azaalkene lactams.

N-O Valence Stabilizer #25: Examples of semicarbazones, bis(semicarbazones), and poly(semicarbazones) (N-O Bidentates, N-O Tetridentates, and N-O Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: acetaldehyde semicarbazone; acetone semicarbazone; pinacolone semicarbazone; benzaldehyde semicarbazone; naphthaldehyde semicarbazone; norbornanone semicarbazone; camphor

semicarbazone; nopinone semicarbazone; 2-pyridinaldehyde semicarbazone; salicylaldehyde semicarbazone; quinolinaldehyde semicarbazone; isatin disemicarbazone; camphorquinone disemicarbazone; camphorquinone disemicarbazone; picolinaldehyde semicarbazone; dipyridyl glyoxal disemicarbazone; di-2-pyridyl ketone semicarbazone; methyl-2-pyridyl ketone semicarbazone; glyoxal disemicarbazone; acetophenone semicarbazone; biacetyl monoxime semicarbazone; acetamidobenzaldehyde semicarbazone; thymolaldosemicarbazone; thiophene-2-aldehyde semicarbazone; phthalaldehyde disemicarbazone; phthalimide disemicarbazone; furaldehyde semicarbazone; naphthoquinone semicarbazone; phenanthrequinone semicarbazone; cyclohexanedione disemicarbazone; ionone semicarbazone; bissemicarbazone of diethyl-3,4-dioxadioate; and lawsone semicarbazone.

N-O Valence Stabilizer #26: Examples of acyl hydrazones, bis(acyl hydrazones), and poly(acyl hydrazones) (N-O Bidentates, N-O Tetridentates, and N-O Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to:

acetaldehyde N-formylhydrazone; acetaldehyde N-benzoylhydrazone; acetone N-formylhydrazone; acetone N-benzoylhydrazone; pinacolone N-formylhydrazone; pinacolone N-benzoylhydrazone; benzaldehyde N-formylhydrazone; benzaldehyde N-benzoylhydrazone; naphthaldehyde N-formylhydrazone; naphthaldehyde N-benzoylhydrazone; norbornanone N-formylhydrazone; norbornanone N-benzoylhydrazone; camphor N-formylhydrazone; camphor N-benzoylhydrazone; nopinone N-formylhydrazone; nopinone N-benzoylhydrazone; 2-pyridinaldehyde N-formylhydrazone; 2-pyridinaldehyde N-benzoylhydrazone; salicylaldehyde N-formylhydrazone; salicylaldehyde N-benzoylhydrazone; quinolinaldehyde N-formylhydrazone; quinolinaldehyde N-benzoylhydrazone; furan-2-aldehyde N-formylhydrazone; furan-2-aldehyde N-benzoylhydrazone; naphthoquinone N-formylhydrazone; naphthoquinone N-benzoylhydrazone; ionone N-formylhydrazone; ionone N-benzoylhydrazone; lawsone N-formylhydrazone; and lawsone N-benzoylhydrazone.

N-O Valence Stabilizer #27: Examples of carbazones (diazene carboxylic hydrazides), bis(carbazones), and poly(carbazones) (N-O Bidentates, N-O Tetridentates, and N-O Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴

include, but are not limited to: diphenylcarbazone; 2-phenylcarbazone; dinaphthylcarbazone; and 2-naphthylcarbazone.

N-O Valence Stabilizer #28: Examples of azo compounds with hydroxyl or carboxy or carbonyl

5 substitution at the ortho- (for aryl) or alpha- or beta- (for alkyl) positions, Bis[o-(HO-)] or alpha- or beta-(HO-)azo compounds], or Poly[o-(HO-)] or alpha- or beta-(HO-)azo compounds) (N-O

Bidentates, N-O Tridentates, N-O Tetridentates, or N-O Hexadentates) that meet the

requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to:

2-hydroxyazobenzene [1-(phenylazo)-2-phenol]; 2,2'-dihydroxyazobenzene (o,o'-

10 dihydroxyazobenzene); (2-furan)azobenzene; Direct Blue 2B; 1-(4-nitrophenylazo)-2-naphthol; 1-(2-hydroxyphenylazo)-2-naphthol; 1-(2-methoxyphenylazo)-2-naphthol; pyridineazo-2-

naphthol (PAN); pyridineazoresorcinol (PAR); 1-phenyl-4-(2-hydroxyphenylazo)-5-pyrazolone;

15 1-phenyl-4-(2-methoxyphenylazo)-5-pyrazolone; o-hydroxy-o'-(beta-

aminoethylamino)azobenzene; 2-hydroxy-2'-methoxymethyleneoxyazobenzene; methyl red;

turquoise blue (reactive blue); sunset yellow; amaranth; tartrazine; Eriochrome Black T;

tropeolins; Allura Red; amaranth; Acid Alizarin Violet N; Acid Blue 29; Acid Orange 8, 63, and 74; Acid Red 1, 4, 8, 37, 88, 97, 114, 151, and 183; Acid Violet 7; Acid Yellow 25, 29, 34, 42,

76, and 99; Brilliant Black BN; Brilliant Crocein; Bordeaux R; Calcion; Chicago Sky Blue;

Chromotrope; Cibacron Brilliant Red; Cibacron Brilliant Yellow; Crocein Orange; Crystal

20 Scarlet; Calmagite; Direct Blue 71; Direct Red 23, 80, and 81; Direct Violet 51; Direct Yellow 8 and 27; Fast Black; Flavazin; Mordant Blue 9; Mordant Brown 1 and 33; Naphthol Blue Black;

New Coccine; Nitrazine Yellow; Nitrosulfonazo III; Orange II; Orange G, OT, and B; Ponceau

3R and SX; Polar Yellow; 2-oxazolylazobenzene; and 2-benzoxazolylazobenzene.

N-O Valence Stabilizer #29: Examples of diazeneformamides, diazeneacetamides,

bis(diazeneformamides), bis(diazeneacetamides), poly(diazeneformamides), and

poly(diazeneacetamides) (N-O Bidentates, N-O Tetridentates, and N-O Hexadentates) that meet

the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited

to: diazeneformamide, diazeneacetamide, phenyldiazeneformamide, diphenyldiazeneformamide,

30 phenyldiazeneacetamide, and diphenyldiazeneacetamide.

N-O Valence Stabilizer #30: Examples of diazeneformic acids, diazeneacetic acids, bis(diazeneformic acids), bis(diazeneacetic acids), poly(diazeneformic acids), poly(diazeneacetic acids) and derivatives thereof (N-O Bidentates, N-O Tetridentates, N-O Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include; but are not limited to: diazeneformic acid, diazeneacetic acid, phenyldiazeneformic acid, diphenyldiazeneformic acid, phenyldiazeneacetic acid, and diphenyldiazeneacetic acid.

N-O Valence Stabilizer #31: Examples of diazeneformaldehydes, diazeneacetaldehydes, bis(diazeneformaldehydes), bis(diazeneacetaldehydes), poly(diazeneformaldehydes), and poly(diazeneacetaldehydes) (N-O Bidentates, N-O Tetridentates and N-O Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diazeneformaldehyde, diazeneacetaldehyde, phenyldiazeneformaldehyde, diphenyldiazeneformaldehyde, phenyldiazeneacetaldehyde, and diphenyldiazeneacetaldehyde.

N-O Valence Stabilizer #32: Examples of diazenediformamides, diazenediacetamides, bis(diazenediformamides), bis(diazenediacetamides), poly(diazenediformamides), and poly(diazenediacetamides) (N-O Tridentates and N-O Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diazenediformamide, diazenediacetamide, diphenyldiazenediformamide, tetraphenyldiazenediformamide, diphenyldiazenediacetamide, and tetraphenyldiazenediacetamide.

N-O Valence Stabilizer #33: Examples of diazenediformic acids, diazenediacetic acids, bis(diazenediformic acids), bis(diazenediacetic acids), poly(diazenediformic acids), poly(diazenediacetic acids) and derivatives thereof (N-O Tridentates and N-O Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diazenediformic acid, diazenediacetic acid, phenyldiazenediformic acid, diphenyldiazenediformic acid, phenyldiazenediacetic acid, and diphenyldiazenediacetic acid.

N-O Valence Stabilizer #34: Examples of diazenediformaldehydes, diazenediacetaldehydes, bis(diazenediformaldehydes), bis(diazenediacetaldehydes), poly(diazenediformaldehydes), and

poly(diazenediacetaldehydes) (N-O Tridentates and N-O Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diazenediformaldehyde, diazenediacetaldehyde, diphenyldiazenediformaldehyde, and diphenyldiazenediacetaldehyde.

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N-O Valence Stabilizer #35: Examples of ortho-hydroxy (or -carboxy) substituted formazans, bis(o-hydroxy or -carboxy substituted formazans), and poly(o-hydroxy or -carboxy substituted formazans) (N-O Bidentates, N-O Tridentates, N-O Tetridentates, and N-O Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 1-(2-hydroxyphenyl)-3,5-diphenylformazan; 1-(2-methoxyphenyl)-3,5-diphenylformazan; 1,5-bis(2-hydroxyphenyl)-3-phenylformazan; and 5-bis(2-methoxyphenyl)-3-phenylformazan.

N-O Valence Stabilizer #36: Examples of ortho-hydroxy (or -carboxy) substituted azines (including ketazines), bis(o-hydroxy or carboxy substituted azines), and poly(o-hydroxy or carboxy substituted azines) (N-O Bidentates, N-O Tridentates, N-O Tetridentates, and N-O Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-hydroxy-1-benzalazine; 2-hydroxy-1-naphthalazine; and 2-hydroxy-1-cyclohexanonazine.

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N-O Valence Stabilizer #37: Examples of Schiff Bases with one Imine (C=N) Group and with ortho- or alpha- or beta-hydroxy or carboxy or carbonyl substitution (N-O Bidentates, N-O Tridentates, N-O Tetridentates, N-O Pentadentates, or N-O Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to:
25 N-(Salicylaldehydo)isopropylamine; N-(2-Furfuralo)isopropylamine; N-(2-Acetylfurano)isopropylamine; N-(2-Hydroxyacetophenono)isopropylamine; N-(Pyridoxalo)isopropylamine; N-(Salicylaldehydo)cyclohexylamine; N-(2-Furfuralo)cyclohexylamine; N-(2-Acetylfurano)cyclohexylamine; N-(2-Hydroxyacetophenono)cyclohexylamine; N-(Pyridoxalo)cyclohexylamine; N-(30 Salicylaldehydo)aniline; N-(2-Furfuralo)aniline (Stenhauz salt); N-(2-Acetylfurano)aniline; N-(2-Hydroxyacetophenono)aniline; N-(Pyridoxalo)aniline; N-(Salicylaldehydo)aminonorbornane;

N-(2-Furfuralo)aminonorbornane; N-(2-Acetylfurano)aminonorbornane; N-(2-Hydroxyacetophenono)aminonorbornane; N-(Pyridoxalo)aminonorbornane; (Salicylaldehydo)anisidine; 2-salicylideneiminobenzothiazole; (Salicylaldehydo)sulfamethazine; N'-histidine-3-methoxysalicylideneimine (V-his); N-(o-carboxybenzaldehydo)-2-aminophenol; 5 N-(salicylaldehydo)isatin; N-(2-furfuralo)isatin; N-(2-acetylfurano)isatin; N-(pyridoxalo)isatin; N-(2-hydroxyacetophenono)isatin; hydrofuranamide; 2-furancarboxaldehyde phenylhydrazone; 2-furancarboxaldehyde 2-pyridyl hydrazone; salicylaldehyde phenylhydrazone; and salicylaldehyde 2-pyridyl hydrazone. Also includes hydrazones with ortho-O substitution.

10 N-O Valence Stabilizer #38: Examples of Schiff Bases with two Imine (C=N) Groups and with ortho- or alpha- or beta-hydroxy or carboxy or carbonyl substitution (N-O Tridentates, N-O Tetridentates, N-O Pentadentates, or N-O Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: N,N'-(2,5-Furandicarboxaldehydo)diisopropylamine; N,N'-(2,5-

15 Furandicarboxaldehydo)dicyclohexylamine; N,N'-(2,5-Furandicarboxaldehydo)dianiline; N,N'-(2,5-Furandicarboxaldehydo)di-aminonorbornane; N,N'-(o-Hydroxyphthalicdialdehydo)diisopropylamine; N,N'-(o-Hydroxyphthalicdialdehydo)dicyclohexylamine; N,N'-(o-Hydroxyphthalicdialdehydo)dianiline; N,N'-(o-Hydroxyphthalicdialdehydo)di-aminonorbornane; N,N'-(o-Hydroxyformylcamphoro)diisopropylamine; N,N'-(o-Hydroxyformylcamphoro)dicyclohexylamine; N,N'-(o-Hydroxyformylcamphoro)dianiline; N,N'-(o-Hydroxyformylcamphoro)di-aminonorbornane; N,N'-(o-Hydroxydiacetylbenzeno)diisopropylamine; N,N'-(o-Hydroxydiacetylbenzeno)dicyclohexylamine; N,N'-(o-Hydroxydiacetylbenzeno)dianiline; N,N'-(3,6-Dihydroxy-1,2-cyclohexanono)diisopropylamine; N,N'-(3,6-Dihydroxy-1,2-cyclohexanono)dicyclohexylamine; N,N'-(3,6-Dihydroxy-1,2-cyclohexanono)dianiline; N,N'-(3,6-Dihydroxy-1,2-cyclohexanono)di-aminonorbornane; N,N'-(2,5-Diacetylfurano)diisopropylamine; N,N'-(2,5-Diacetylfurano)dicyclohexylamine; N,N'-(2,5-Diacetylfurano)dianiline; N,N'-(2,5-Diacetylfurano)di-aminonorbornane; N,N'-(Salicylaldehydo)ethylenediamine; N,N'-(o-Hydroxynaphthaldehydo)ethylenediamine; N,N'-(o-Hydroxyacetophenono)ethylenediamine; ;

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N,N'-(Salicylaldehydo)trimethylenediamine; N,N'-(o-Hydroxynaphthaldehydo)trimethylenediamine; N,N'-(o-Hydroxyacetophenono)trimethylenediamine; ; N,N'-(Salicylaldehydo)cyclohexane-1,2-diamine; N,N'-(o-Hydroxynaphthaldehydo)cyclohexane-1,2-diamine; N,N'-(o-Hydroxyacetophenono)cyclohexane-1,2-diamine; N,N'-(Salicylaldehydo)-1,2-diaminobenzene; N,N'-(o-Hydroxynaphthaldehydo)-1,2-diaminobenzene; N,N'-(o-Hydroxyacetophenono)-1,2-diaminobenzene; N,N'-bis(salicylaldehydo)-1,12-diaminododecane (Saldn); N,N'-bis(3-methoxysalicylaldehydo)-o-phenyldiamine; N,N'-bis(3,4-difluorobenzaldehydo)-4,4'-benzidine; and N,N'-phenylenebis(3-methoxysalicylideneimine) (V-ph-V). Also includes hydrazones with
ortho-O substitution.

N-O Valence Stabilizer #39: Examples of Schiff Bases with three Imine (C=N) Groups and with ortho- or alpha- or beta-hydroxy or carboxy or carbonyl substitution (N-O Tetridentates, N-O Pentadentates, or N-O Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: N,N',N''-(Salicylaldehydo)tris(2-aminoethyl)amine; N,N',N''-(o-Hydroxynaphthaldehydo)tris(2-aminoethyl)amine; and N,N',N''-(o-Hydroxyacetophenono)tris(2-aminoethyl)amine. Also includes hydrazones with ortho-O substitution.

N-O Valence Stabilizer #40: Examples of silyl aminoalcohols (N-O Bidentates, N-O Tridentates, N-O Tetridentates, and N-O Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: silatranes.

N-O Valence Stabilizer #41: Examples of hydroxyalkyl imines (imino alcohols) (N-O Bidentates, N-O Tridentates, N-O Tetridentates, and N-O Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-hydroxycyclohexylimine; 3-hydroxy-2-iminonorbornane; 2,2'-diiminodicyclohexyl ether; oxamide; 3-imino-1,5-pentanodialdehyde; iminodiacetic acid; and iminodipropionic acid.

N-O Valence Stabilizer #42: Examples of hydroxyaryl amines and hydroxyaryl imines (N-O Bidentates, N-O Tridentates, N-O Tetridentates, and N-O Hexadentates) that meet the

requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to:
2-aminophenol; 2-aminobenzoic acid (anthranilic acid); 2-aminoanisole; o-phenetidine; o-anisidine; 2-hydroxymethyl)-alpha-aminotoluene; 1-amino-2-naphthol; 2-amino-1-naphthol; 2,2'-di(aminomethyl)diphenylketone; isophoronediamine; tris-2,4,6-dimethylaminomethyl phenol; di(2-amino)phenyl ether; 1,3-di(2-amino)phenyl-2-hydroxypropane; 1,3-di(3-amino)phenyl-2-hydroxypropane; 1,3-di(2-hydroxy)phenyl-2-aminopropane; 1,3-di(3-hydroxy)phenyl-2-aminopropane; 2,2'-dihydroxyiminodibenzyl; 2,2'-iminodibenzoic acid; 2,2'-dihydroxyiminostilbene; poly(o-phenetidine); poly(o-aminophenol); poly(o-anisidine); and 3-(anilino)propionamide.

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N-O Valence Stabilizer #43: Examples of five-membered heterocyclic rings containing one, two, three, or four nitrogen atoms at least one additional oxygen atom binding site not in a ring (N-O Bidentates, N-O Tridentates, N-O Tetridentates, or N-O Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to:

15 2-hydroxypyrrrole; 2-(methylhydroxy)methylpyrrole; 2,5-(hydroxymethyl)pyrrole; 2,5-(methylhydroxymethyl)pyrrole; imidazoline-2-one (2-hydroxyimidazole); 2-hydroxythiazoline; 2-hydroxybenzimidazole; 2-hydroxybenzothiazole; 2-hydroxybenzoxazole; 2-hydantoin; di-2-pyridylglyoxal (2,2'-pyridil); bis((1-pyrazolyl)methane)ether; bis(2-(1-pyrazolyl)ethane)ether; bis(benzimidazolylmethane)ether; bis(benzimidazolylethane)ether; tris(imidazolyl)methanol; 20 tris(imidazolylmethane)methanol; N-hydroxymethyl-N,N-(benzimidazolylmethane)amine; N-(2-hydroxyethyl)-N,N-(benzimidazolylmethane)amine; N,N'-di(benzimidazolylmethane)-1,3-diamino-2-hydroxypropane; N,N,N',N'-tetrakis(benzimidazolylmethane)-1,3-diamino-2-hydroxypropane; bis(N,N-((4-imidazolyl)methane)2-aminoethane)ether; 4-carboxybenzotriazole; antipyrine; 4-aminoantipyrine (aap); hydantoin; aminoalkylhydantoins; 2,5-oxazolidinedione; 25 benzylbibenzoyltriazole (bdbt); 5-hydroxymethylimidazole; dicarboxyalkylbenzotriazoles; bis(hydroxyphenyl)aminotriazoles; pyrrole-2-carboxaldehyde; (oxopyrrolidinylalkyl)triazoles; alkoxybenzotriazoles; aryloxybenzotriazoles; 3-salicylamido-4,5-dihydro-1,2,4-triazole; 5-(alkoxy)benzotriazole; (polyoxyalkylene)oxazolidines; 1-(dialkylaminomethyl)-5-carboxyalkylbenzotriazole; 1-(2-hydroxyethyl)imidazoline; 1-acetoxyimidazole; 1-acetylimidazole; benzotriazolecarboxylic acid; poly(oxyalkylated)pyrazoles; 30 poly(oxyalkylated)thiadiazoles; 1,2,4-triazole-3-carboxylic acid; 5-hydroxypyrazole; 3-phenyl-

1,2,4-triazol-5-one (ptr); 1-acetylbenzimidazole; 1-[(acetoxyl)ethyl]benzimidazole; creatinine; indole-2-carboxylic acid; pyrrole-2-carboxylic acid; imidazole-2-carboxylic acid; pyrazole-2-carboxylic acid; and 1,1'-oxalyldiimidazole.

- 5 N-O Valence Stabilizer #44: Examples of six-membered heterocyclic rings containing one, two, three, or four nitrogen atoms at least one additional oxygen atom binding site not in a ring (N-O Bidentates, N-O Tridentates, N-O Tetridentates, or N-O Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 4-aminomethyl-3-pyridinemethanol (including pyridoxamine); 2-hydroxypyridine; 2-(methylhydroxy)methylpyridine; 2-(2-(methylhydroxy)ethyl)pyridine; 2,6-(hydroxymethyl)pyridine; 2,6-(methylhydroxymethyl)pyridine; 2-hydroxypyrimidine; 2-dihydroxymethylpyrimidine; 2-hydroxyquinoline; 8-hydroxyquinoline (oxine); 8-methylhydroxyquinoline; 2-hydroxyquinazoline; orotic acid (1,2,3,6-tetrahydro-2,6-dioxo-4-pyrimidinecarboxylic acid) (6-uracilcarboxylic acid); 1-methylpyrimidine-2-one; uracil; 6-hydroxypurine; bis(N,N,N',N'-tetra(2-(2-pyridyl)ethane)aminomethane)ether; bis(N,N,N',N'-tetra(2-(2-pyridyl)ethane)aminoethane)ether; quinazol-4-one; quinazol-2-one; 5-azathymine; 2-hydroxybenzimidazole (2-hbz); guanine; 1,3,5-triazin-6-one; 6-hydroxy-1,3,5-triazine; 4,6-dihydroxy-1,3,5-triazine; triazine carboxylic acids; 2,3-dihydroxypyridine; thiomorpholin-3-one; hydroxytetrahydropyrimidines; 2-piperazinones; 2-piperdinones; dilituric acid; actinoquinol; 20 caffeine; citrazinic acid; picolinic acid; 2-quinolol; 2,6-dimethoxypyridine; quinoxaline-2-carboxylic acid; flucytosine; hypoxanthine; hexamethylolmelamine; hydroorotic acid; isoorotic acid; xanthine; leucopterin; nitroorotic acid; 8-azaguanine; and cyanuric acid.

- 25 N-O Valence Stabilizer #45: Examples of five-membered heterocyclic rings containing one or two oxygen atoms at least one additional nitrogen atom binding site not in a ring (N-O Bidentates, N-O Tridentates, N-O Tetridentates, or N-O Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-aminofuran; 2,5-diaminofuran; 2-aminomethylfuran; 2,5-di(aminomethyl)furan; 2-aminobenzofuran; and 2-amino-1,3-dioxolane.

N-O Valence Stabilizer #46: Examples of six-membered heterocyclic rings containing one or two oxygen atoms at least one additional nitrogen atom binding site not in a ring (N-O Bidentates, N-O Tridentates, N-O Tetridentates, or N-O Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to:
5 2-aminopyran; 2,6-diaminopyran; 2-aminomethylpyran; 2,6-di(aminomethyl)pyran; and 2-aminobenzopyran.

N-O Valence Stabilizer #47: Examples of five-membered heterocyclic rings containing one, two, three, or four nitrogen atoms at least one additional oxygen atom binding site in a separate ring
10 (N-O Bidentates, N-O Tridentates, N-O Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-(2-furan)pyrrole; 2,5-di(2-furan)pyrrole; 2-(2-pyran)pyrrole; 2,5-di(2-pyran)pyrrole; 2,5-di(2-pyrrole)furan; and 2,6-di(2-pyrrole)pyran.

15 N-O Valence Stabilizer #48: Examples of six-membered heterocyclic rings containing one, two, three, or four nitrogen atoms at least one additional oxygen atom binding site in a separate ring (N-O Bidentates, N-O Tridentates, N-O Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-(2-furan)pyridine; 2,6-di(2-furan)pyridine; 2-(2-pyran)pyridine; 2,6-di(2-pyran)pyridine; 2,5-di(2-pyridyl)furan; 2,6-di(2-pyridyl)pyran; and drometizole.
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25 N-O Valence Stabilizer #49: Examples of two-, three-, four-, six-, eight-, and ten-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of nitrogen (usually amine or imine groups) or oxygen (usually hydroxy, carboxy, or carbonyl groups) and are not contained in component heterocyclic rings (N-O Bidentates, N-O Tridentates, N-O Tetridentates, and N-O Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: azaoxacyclobutane ([4]aneNO); azaoxacyclopentane ([5]aneNO); azaoxacyclohexane ([6]aneNO); azaoxacycloheptane ([7]aneNO); azaoxacyclooctane ([8]aneNO); azaoxacyclobutene ([4]eneNO); azaoxacyclopentene ([5]eneNO); azaoxacyclohexene ([6]eneNO); azaoxacycloheptene ([7]eneNO); azaoxacyclooctene
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([8]eneNO); azaoxacyclobutadiene ([4]dieneNO); azaoxacyclopentadiene ([5]dieneNO); azaoxacyclohexadiene ([6]dieneNO); azaoxacycloheptadiene ([7]dieneNO); azaoxacyclooctadiene ([8]dieneNO); diazaoxacyclohexane ([6]aneON₂); diazaoxacycloheptane ([7]aneON₂); diazaoxacyclooctane ([8]aneON₂); diazaoxacyclononane ([9]aneON₂);
5 diazaoxacyclodecane ([10]aneON₂); diazaoxacycloundecane ([11]aneON₂); diazaoxacyclododecane ([12]aneON₂); diazaoxacyclohexene ([6]eneON₂); diazaoxacycloheptene ([7]eneON₂); diazaoxacyclooctene ([8]eneON₂); diazaoxacyclononene ([9]eneON₂); diazaoxacyclodecene ([10]eneON₂); diazaoxacycloundecene ([11]eneON₂); diazaoxacyclododecene ([12]eneON₂); diazadioxacyclooctane ([8]aneO₂N₂);
10 diazadioxacyclononane ([9]aneO₂N₂); diazadioxacyclodecane ([10]aneO₂N₂); diazadioxacycloundecane ([11]aneO₂N₂); diazadioxacyclododecane ([12]aneO₂N₂); diazadioxacyclotridecane ([13]aneO₂N₂); diazadioxacyclotetradecane ([14]aneO₂N₂); diazadioxacyclopentadecane ([15]aneO₂N₂); diazadioxacyclohexadecane ([16]aneO₂N₂); diazadioxacycloheptadecane ([17]aneO₂N₂); diazadioxacyclooctadecane ([18]aneO₂N₂);
15 diazadioxacyclononadecane ([19]aneO₂N₂); diazadioxacycloicosane ([20]aneO₂N₂); diazadioxacyclooctadiene ([8]dieneO₂N₂); diazadioxacyclononadiene ([9]dieneO₂N₂); diazadioxacyclodecadiene ([10]dieneO₂N₂); diazadioxacycloundecadiene ([11]dieneO₂N₂); diazadioxacyclododecadiene ([12]dieneO₂N₂); diazadioxacyclotridecadiene ([13]dieneO₂N₂); diazadioxacyclotetradecadiene ([14]dieneO₂N₂); diazadioxacyclopentadecadiene
20 ([15]dieneO₂N₂); diazadioxacyclohexadecadiene ([16]dieneO₂N₂); diazadioxacycloheptadecadiene ([17]dieneO₂N₂); diazadioxacyclooctadecadiene ([18]dieneO₂N₂); diazadioxacyclononadecadiene ([19]dieneO₂N₂); and diazadioxacycloicosadiene ([20]dieneO₂N₂).

25 N-O Valence Stabilizer #50: Examples of four-, six-, eight-, or ten-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of nitrogen or oxygen and are contained in component heterocyclic rings (N-O Bidentates, N-O Tridentates, N-O Tetridentates, or N-O Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴
30 include, but are not limited to: dipyrandipyridines; difurandipyrroles; tripyrantripyridines; trifurantripyrrroles; tetrapyrantrapyridines; and tetrafurantrapyrrroles.

N-O Valence Stabilizer #51: Examples of four-, six-, eight-, or ten-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of nitrogen or oxygen and are contained in a combination of heterocyclic rings and amine, imine, hydroxy, carboxy, or carbonyl groups (N-O Bidentates, N-O Tridentates, N-O Tetridentates, or N-O Hexadentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: azaoxatetraphyrins; diazadioxatetraphyrins; azaoxahexaphyrins; diazadioxahexaphyrins; and triazatrioxahexaphyrins.

10 S-O Valence Stabilizer #1: Examples of 1,3-monothioketones (monothio-beta-ketonates), 1,3,5-monothioketones, 1,3,5-dithioketones, bis(1,3-monothioketones), and poly(1,3-

monothioketones) (S-O Bidentates, S-O Tridentates, S-O Tetridentates) that meet the

requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: hexafluoropenta-2-thione-4-ketone; 1,3-diphenyl-1,3-propana-1-thione-3-ketone;

15 benzoylthiopinacolone; cyclohexoylthiocyclohexoylmethane; diphenylpentanedithionate;

tetramethylnonanedithionate; hexafluoroheptanedithionate; trifluoroheptanedithionate; 1-(2-

thienyl)-butan-1-thione-3-ketone, 1-(2-naphthyl)-butan-1-thione-3-ketone, and

trifluoroacetylthiocamphor.

20 S-O Valence Stabilizer #2: Examples of thiomalonamides (thiomalonodiamides),

bis(thiomalonamides), and polythiomalonamides (S-O Bidentates, S-O Tridentates, S-O

Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴

include, but are not limited to: thiomalonamide, N-phenylthiomalonamide, N-

25 benzylthiomalonamide, N-pentafluorophenylthiomalonamide, N-cyclohexylthiomalonamide, N-

-norbornylthiomalonamide, N,N'-diphenylthiomalonamide, N,N'-dibenzylthiomalonamide, N,N'-

dipentafluorophenylthiomalonamide, N,N'-dicyclohexylthiomalonamide, and N,N'-

norbornylthiomalonamide.

30 S-O Valence Stabilizer #3: Examples of 2-thioacylacetamides, 2-acylthioacetamides, bis(2-

thioacylacetamides), bis(2acylthioacetamides), poly(2-thioacylacetamides), and poly(2-

Acylthioacetamides) (S-O Bidentates, S-O Tridentates, S-O Tetridentates) that meet the

requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to:
2-acetothioacetamide, 2-thioacetoacetamide, N-phenyl-2-acetothioacetamide, N-
pentafluorophenyl-2-acetothioacetamide, N-benzyl-2-acetothioacetamide, N-cyclohexyl-2-
acetothioacetamide, N-norbornyl-2-acetothioacetamide, N-phenyl-2-benzothioacetamide, N-
5 pentafluorophenyl-2-pentafluorobenzothioacetamide, and N-cyclohexyl-2-
cyclohexothioacetamide.

S-O Valence Stabilizer #4: Examples of dithiodicarbonic diamides, bis(dithiodicarbonic
diamides), and poly(dithiodicarbonic diamides) (S-O Bidentates, S-O Tridentates, S-O
10 Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴
include, but are not limited to: dithiodicarbonic diamide; N-phenyldithiodicarbonic diamide; N-
pentafluorophenyldithiodicarbonic diamide; N-benzyldithiodicarbonic diamide; N-
cyclohexyldithiodicarbonic diamide; N-norbornyldithiodicarbonic diamide; N,N'-
diphenyldithiodicarbonic diamide; N,N'-dipentafluorophenyldithiodicarbonic diamide; N,N'-
15 dibenzyldithiodicarbonic diamide; N,N'-dicyclohexyldithiodicarbonic diamide; and N,N'-
dinorbornyldithiodicarbonic diamide.

S-O Valence Stabilizer #5: Examples of monothiohypophosphoric acids,
bis(monothiohypophosphoric acids), poly(monothiohypophosphoric acids), and derivatives
20 thereof (S-O Bidentates, S-O Tridentates, S-O Tetridentates) that meet the requirements for use
as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to:
monothiohypophosphoric acid, methylmonothiohypophosphoric acid,
isopropylmonothiohypophosphoric acid, tert-butylmonothiohypophosphoric acid,
phenylmonothiohypophosphoric acid, pentafluorophenylmonothiohypophosphoric acid,
25 benzylmonothiohypophosphoric acid, cyclohexylmonothiohypophosphoric acid,
norbornylmonothiohypophosphoric acid, dimethylmonothiohypophosphoric acid,
diisopropylmonothiohypophosphoric acid, di-tert-butylmonothiohypophosphoric acid,
diphenylmonothiohypophosphoric acid, di-pentafluorophenylmonothiohypophosphoric acid,
30 dibenzylmonothiohypophosphoric acid, dicyclohexylmonothiohypophosphoric acid, and
dinorbornylmonothiohypophosphoric acid.

S-O Valence Stabilizer #6: Examples of monothiohypophosphoramides, bis(monothiohypophosphoramides), and poly(monothiohypophosphoramides) (S-O Bidentates, S-O Tridentates, S-O Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: monothiohypophosphamide, N-methylmonothiohypophosphamide, N-isopropylmonothiohypophosphamide, N-tert-butylmonothiohypophosphamide, N-phenylmonothiohypophosphamide, N-pentafluorophenylmonothiohypophosphamide, N-benzylmonothiohypophosphamide, N-cyclohexylmonothiohypophosphamide, N-norbornylmonothiohypophosphamide, N,N''-dimethylmonothiohypophosphamide, N,N''-diisopropylmonothiohypophosphamide, N,N''-di-tert-butylmonothiohypophosphamide, N,N''-diphenylmonothiohypophosphamide, N,N''-di-pentafluorophenylmonothiohypophosphamide, N,N''-dibenzylmonothiohypophosphamide, N,N''-dicyclohexylmonothiohypophosphamide, and N,N''-dinorbornylmonothiohypophosphamide.

S-O Valence Stabilizer #7: Examples of monothioimidodiphosphoric acids, monothiohydrazidodiphosphoric acids, bis(monothioimidodiphosphoric acids), bis(monothiohydrazidodiphosphoric acids), poly(monothioimidodiphosphoric acids), poly(monothiohydrazidodiphosphoric acids), and derivatives thereof (S-O Bidentates, S-O Tridentates, S-O Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: monothioimidodiphosphoric acid, methylmonothioimidodiphosphoric acid, isopropylmonothioimidodiphosphoric acid, tert-butylmonothioimidodiphosphoric acid, phenylmonothioimidodiphosphoric acid, pentafluorophenylmonothioimidodiphosphoric acid, benzylmonothioimidodiphosphoric acid, cyclohexylmonothioimidodiphosphoric acid, norbornylmonothioimidodiphosphoric acid, dimethylmonothioimidodiphosphoric acid, diisopropylmonothioimidodiphosphoric acid, di-tert-butylmonothioimidodiphosphoric acid, diphenylmonothioimidodiphosphoric acid, di-pentafluorophenylmonothioimidodiphosphoric acid, dibenzylmonothioimidodiphosphoric acid, dicyclohexylmonothioimidodiphosphoric acid, and dinorbornylmonothioimidodiphosphoric acid.

S-O Valence Stabilizer #8: Examples of monothioimidodiphosphoramides, monothiohydrazidodiphosphoramides, bis(monothioimidodiphosphoramides),

bis(monothiohydrazidodiphosphoramides), poly(monothioimidodiphosphoramides), and poly(monothiohydrazidodiphosphoramides) (S-O Bidentates, S-O Tridentates, S-O Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: monothioimidodiphosphoramide, N-
5 methylmonothioimidodiphosphoramide, N-isopropylmonothioimidodiphosphoramide, N-tert-butylmonothioimidodiphosphoramide, N-phenylmonothioimidodiphosphoramide, N-pentafluorophenylmonothioimidodiphosphoramide, N-benzylmonothioimidodiphosphoramide, N-cyclohexylmonothioimidodiphosphoramide, N-norbornylmonothioimidodiphosphoramide, N,N''-dimethylmonothioimidodiphosphoramide, N,N''-
10 diisopropylmonothioimidodiphosphoramide, N,N''-di-tert-butylmonothioimidodiphosphoramide, N,N''-diphenylmonothioimidodiphosphoramide, N,N''-di-pentafluorophenylmonothioimidodiphosphoramide, N,N''-dibenzylmonothioimidodiphosphoramide, N,N''-dicyclohexylmonothioimidodiphosphoramide, and N,N''-dinorbornylmonothioimidodiphosphoramide.
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S-O Valence Stabilizer #9: Examples of monothiodiphosphoramides, bis(monothiodiphosphoramides), and poly(monothiodiphosphoramides) (S-O Bidentates, S-O Tridentates, S-O Tetridentates) that meet the requirements for use as “wide band” valence stabilizers for Ce⁺⁴ include, but are not limited to: monothiodiphosphoramide, N-
20 methylmonothiodiphosphoramide, N-isopropylmonothiodiphosphoramide, N-tert-butylmonothiodiphosphoramide, N-phenylmonothiodiphosphoramide, N-pentafluorophenylmonothiodiphosphoramide, N-benzylmonothiodiphosphoramide, N-cyclohexylmonothiodiphosphoramide, N-norbornylmonothiodiphosphoramide, N,N''-dimethylmonothiodiphosphoramide, N,N''-diisopropylmonothiodiphosphoramide, N,N''-di-
25 tert-butylmonothiodiphosphoramide, N,N''-diphenylmonothiodiphosphoramide, N,N''-di-pentafluorophenylmonothiodiphosphoramide, N,N''-dibenzylmonothiodiphosphoramide, N,N''-dicyclohexylmonothiodiphosphoramide, and N,N''-dinorbornylmonothiodiphosphoramide.

S-O Valence Stabilizer #10: Examples of monothiodiphosphoric acids, bis(monothiodiphosphoric acids), poly(monothiodiphosphoric acids), and derivatives thereof (S-O Bidentates, S-O Tridentates, S-O Tetridentates) that meet the requirements for use as “wide

band" valence stabilizers for Ce⁺⁴ include, but are not limited to: monothiodiphosphoric acid, methylmonothiodiphosphoric acid, isopropylmonothiodiphosphoric acid, tert-butylmonothiodiphosphoric acid, phenylmonothiodiphosphoric acid, pentafluorophenylmonothiodiphosphoric acid, benzylmonothiodiphosphoric acid, cyclohexylmonothiodiphosphoric acid, norbornylmonothiodiphosphoric acid, dimethylmonothiodiphosphoric acid, diisopropylmonothiodiphosphoric acid, di-tert-butylmonothiodiphosphoric acid, diphenylmonothiodiphosphoric acid, di-pentafluorophenylmonothiodiphosphoric acid, dibenzylmonothiodiphosphoric acid, dicyclohexylmonothiodiphosphoric acid, and dinorbornylmonothiodiphosphoric acid.

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S-O Valence Stabilizer #11: Examples of monothiocarbamates, bis(monothiocarbamates), and poly(monothiocarbamates) (including N-hydroxymonothiocarbamates and N-mercaptomonothiocarbamates) (S-O Bidentates, S-O Tridentates, and S-O Tetridentates) that meet the requirements for use as "wide band" valence stabilizers for Ce⁺⁴ include, but are not limited to: dimethylmonothiocarbamate (dmmtc); di(trifluorodimethyl)monothiocarbamate; diethylmonothiocarbamate (demtc); dipropylmonothiocarbamate; diisopropylmonothiocarbamate; dibutylmonothiocarbamate; ditertbutylmonothiocarbamate; dicyanamidomonothiocarbamate; diphenylmonothiocarbamate; di(pentafluorophenyl)monothiocarbamate; dibenzylmonothiocarbamate; dinaphthylmonothiocarbamate; dicyclohexylmonothiocarbamate; dinorbornylmonothiocarbamate; diadamantylmonothiocarbamate; pyrrolidinomonothiocarbamate (pyrmtc); piperidinomonothiocarbamate (pipmtc); morpholinomonothiocarbamate (mormtc); thiamorpholinomonothiocarbamate; 3-pyrrolinomonothiocarbamate; pyrrolomonothiocarbamate; oxazolomonothiocarbamate; isoxazolomonothiocarbamate; thiazolomonothiocarbamate; isothiazolomonothiocarbamate; indolomonothiocarbamate; carbazolomonothiocarbamate; pyrazolinomonothiocarbamate; imidazolinomonothiocarbamate; pyrazolomonothiocarbamate; imidazolomonothiocarbamate; indazolomonothiocarbamate; and triazolomonothiocarbamate.

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Water-soluble precursors for the organic valence stabilizers are typically used to ensure that sufficient material is available for coating deposition from aqueous solutions. Identification of suitable water-soluble precursors can be difficult because many of these organics do not form a wide range of water-soluble compounds.

As with the inorganic valence stabilizers, crosses between two or more organic valence stabilizers can be used to stabilize Ce^{+4} for corrosion protection. For example, in some instances it may be desirable to form a valence stabilizer out of a beta-diketone and an amine ligand. Both of these materials can complex to form a mixed beta-diketone/amine valence stabilizer out of the conversion coating solution during the coating process.

10 4c) Narrow Band Inorganic Valence Stabilizers for Ce^{+4}

Narrow band valence stabilizers can be used to stabilize Ce^{+4} for corrosion protection, but they are less typical. Narrow band valence stabilizers exhibit some limitation in their use when compared to wide band stabilizers. They may be toxic or may complex Ce^{+4} only with difficulty. 15 These narrow band stabilizers include, but are not limited to, bismuthates, germanates, arsenates, and selenates. For example, valence stabilizers using arsenate are less desirable because their inherent toxicity is very large (greater than hexavalent chromium), although they may be very effective at inhibiting corrosion when used with Ce^{+4} . Arsenates can be used as valence stabilizers for Ce^{+4} when the toxicity of the coating solution is not a factor in its use.

20 Other narrow band stabilizers may result in Ce^{+4} -stabilizer complexes with limited stability, an undesirable solubility range, or limited electrostatic characteristics, and they would be useful only in limited applications. Formation of a protective shell of octahedra or icosahedra with borates (B^{+3}), aluminates (Al^{+3}), silicates (Si^{+4}) titanates (Ti^{+4}), or zirconates (Zr^{+4}) around the Ce^{+4} ion is difficult but possible. These compounds are known to form octahedra or 25 icosahedra, but tend to polymerize in chain-like structures when precipitated from aqueous solution under ambient conditions. These and other narrow band stabilizers can provide some degree of corrosion protection when complexed with Ce^{+4} , but will not necessarily perform with the same efficiency as the wide band stabilizers by themselves. Combinations of these materials, such as phosphosilicates, aluminosilicates, or borosilicates may also function as narrow band 30 inorganic valence stabilizers.

Narrow band inorganic stabilizers used in combination with wide band inorganic stabilizers described above can be used to provide significant corrosion protection. Conversely, modifications of wide band inorganic valence stabilizers can result in a complex with reduced corrosion inhibition. For example, heteropolytungstates can contain ions in addition to the desired Ce⁺⁴ ion.

The central cavity of the heteropolytungstates can contain ions in addition to the desired Ce⁺⁴ ion. For example, the use of silicomolybdates, phosphomolybdates, silicotungstates, and phosphotungstates is possible. In these Ce⁺⁴-valence stabilizer complexes, Si⁺⁴ or P⁺⁵ ions also occupy the central cavity of the complex with the Ce⁺⁴ ion. The inclusion of additional ions in the central cavity reduces the stability of the complex, and thereby leads to lower corrosion protection. Nonetheless, these complexes also demonstrated some corrosion-inhibiting activity.

The additional ions that can be included within the central cavity of the heteropolytungstates described above depend upon the size of the central cavity, which in turn depend upon the specific chemistry exhibited by an inorganic valence stabilizer (e.g., molybdate, tungstate, periodate, carbonate, etc.). In general, these additional ions must also be small so as to ensure the stability of the formed Ce⁺⁴-valence stabilized complex. Examples of small additional ions include, but are not limited to: B⁺³, Al⁺³, Si⁺⁴, P⁺⁵, Ti⁺⁴, V⁺⁵, V⁺⁴, Cr⁺⁶, Cr⁺⁴, Cr⁺³, Mn⁺⁴, Mn⁺³, Mn⁺², Fe⁺³, Fe⁺², Co⁺², Co⁺³, Ni⁺², Ni⁺³, Ni⁺⁴, Cu⁺², Cu⁺³, Zn⁺², Ga⁺³, Ge⁺⁴, As⁺⁵, As⁺³, and Zr⁺⁴.

Water-soluble precursors for these materials are desirable. Typically, the free acids (e.g., silicomolybdic acid, phosphotungstic acid, borotungstic acid, etc.) offer the most water-soluble precursors for these materials.

4d) Narrow Band Organic Valence Stabilizers for Ce⁺⁴

Narrow band organic valence stabilizers include those general classes of chemical compounds that result in Ce⁺⁴-valence stabilizer complexes that are either less stable, more soluble in water, or more toxic than the wide band organic stabilizers. Some of the typical “narrow band” organic valence stabilizer species are listed in Table 2 below.

Table 2. Narrow Band Organic Valence Stabilizers for the Ce⁺⁴ Ion

General Structural Name (Type of Organic)	Structural Representation
<u>N Valence Stabilizer #1:</u> Five-, Seven-, or Nine-Membered Macrocyclics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Nitrogen (usually amine or imine groups) and are not contained in Component Heterocyclic Rings (N-N Tridentates, N-N Tetridentates, and N-N Hexadentates)	Macroyclic ligands containing five, seven, or nine nitrogen binding sites to valence stabilize the central metal ion. Can include other hydrocarbon or ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbons/rings may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>N Valence Stabilizer #2:</u> Five-, or Seven-Membered Macrocyclics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Nitrogen and are contained in Component 5-Membered Heterocyclic Rings (N-N Tridentates, N-N Tetridentates, or N-N Hexadentates)	Macroyclic ligands containing a total of five or seven five-membered heterocyclic rings containing nitrogen binding sites. Can include other hydrocarbon/ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbon/rings may or may not have halogen or polarizing or water-insolubilizing groups attached.
<u>N Valence Stabilizer #3:</u> Five-, Seven-, or Nine-Membered Macrocyclics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Nitrogen and are contained in a Combination of 5-Membered Heterocyclic Rings and Amine or Imine Groups (N-N Tridentates, N-N Tetridentates, or N-N Hexadentates)	Macroyclic ligands containing at least one 5-membered heterocyclic ring. These heterocyclic rings provide nitrogen binding sites to valence stabilize the central metal ion. Other amine or imine binding sites can also be included in the macrocyclic ligand, so long as the total number of binding sites is five, seven, or nine. Can include other hydrocarbon/ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbon/rings may or may not have halogen or polarizing or water-insolubilizing groups attached.
<u>N Valence Stabilizer #4:</u> Five- or Seven-Membered Macrocyclics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Nitrogen and are contained in Component 6-	Macroyclic ligands containing a total of five or seven six-membered heterocyclic rings containing nitrogen binding sites. Can include other hydrocarbon/ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating

Membered Heterocyclic Rings (N-N Tridentates, N-N Tetridentates, or N-N Hexadentates)	hydrocarbon/rings may or may not have halogen or polarizing or water-insolubilizing groups attached.
<u>N Valence Stabilizer #5:</u> Five-, Seven-, or Nine-Membered Macrocyclics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Nitrogen and are contained in a Combination of 6-Membered Heterocyclic Rings and Amine or Imine Groups (N-N Tridentates, N-N Tetridentates, or N-N Hexadentates)	Macroyclic ligands containing at least one 6-membered heterocyclic ring. These heterocyclic rings provide nitrogen binding sites to valence stabilize the central metal ion. Other amine or imine binding sites can also be included in the macrocyclic ligand, so long as the total number of binding sites is five, seven, or nine. Can include other hydrocarbon/ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbon/rings may or may not have halogen or polarizing or water-insolubilizing groups attached.
<u>N Valence Stabilizer #6:</u> Silylamines and Silazanes, including Macroyclic Derivatives, wherein at least one Nitrogen Atom is a Binding Site (N Monodentates, N-N Bidentates, N-N Tridentates, N-N Tetridentates, and N-N Hexadentates)	$\text{N}(\text{SiR}_3)_3$, $\text{R}'\text{N}(\text{SiR}_3)_2$, or $\text{R}'\text{R}''\text{N}(\text{SiR}_3)$ for silylamines; and $[\text{RR}''\text{Si}-\text{NR}']_x$ ($x = 1-10$) for silazanes where R, R', and R'' represents H or any organic functional group wherein the number of carbon atoms ranges from 0 to 35, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, P, As, O, S, or Se atoms.
<u>N Valence Stabilizer #7:</u> Guanidines, Diguanidines, and Polyguanidines (N-N Bidentates, N-N Tridentates, N-N Tetridentates, and N-N Hexadentates)	$\text{RR}'-\text{N}-\text{C}(=\text{NH})\text{NR}''\text{R}'''$, where R, R', R'', and R''' represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N Valence Stabilizer #8:</u> Phosphonitrile Amides, and Bis(phosphonitrile amides) (N-N Bidentates, N-N Tetridentates)	$\text{RR}'-\text{N}-\text{P}(\equiv\text{N})-\text{N}-\text{R}''\text{R}'''$, where R, R', R'', and R''' represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N Valence Stabilizer #9:</u> Phosphonimidic Diamides, Bis(Phosphonimidic Diamides), and Poly(Phosphonimidic Diamides) (N-N Bidentates, N-N Tetridentates)	$(\text{NH}=\text{PR}''''(-\text{NRR}')(-\text{NR}''\text{R}'''))$, where R, R', R'', R''', and R'''' represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached.

	Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N Valence Stabilizer #10:</u> Phosphonamidimidic Acid, Phosphonamidimidothioic Acid, Bis(Phosphonamidimidic Acid), Bis(Phosphonamidimidothioic Acid), Poly(Phosphonamidimidic Acid), Poly(Phosphonamidimidothioic Acid), and derivatives thereof (N-N Bidentates, and N-N Tetridentates)	(NH=)PR'''(-NRR')(-OR") for phosphonamidimidic acid and (NH=)PR'''(-NRR')(-SR") for phosphonamidimidothioic acid, where R, R', R", and R''' represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N Valence Stabilizer #11:</u> Pyridinaldimines, Bis(pyridinaldimines), and Poly(pyridinaldimines) (N-N Bidentates, N-N Tridentates, and N-N Tetridentates)	C ₅ H ₅ N-CR'=NR', where C ₅ H ₅ N is a pyridine derivative, R is typically an aromatic constituent (i.e., -C ₆ H ₅), and R' represents H or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N Valence Stabilizer #12:</u> Hydrazones, Bis(hydrazones), and Poly(hydrazones) (N Monodentates, N-N Bidentates, N-N Tridentates, and N-N Tetridentates)	R-NH-N=R', where R and R' represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. (Either R or R' is typically an aryl group.) Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N Valence Stabilizer #13:</u> Azo compounds including triazenes without chelate substitution at the ortho- (for aryl) or alpha- or beta- (for alkyl) positions, Bis(azo compounds), or Poly(azo compounds) (N Monodentates, N-N Bidentates, or N-N-N Tridentates)	R-N=N-R' for azo compounds, R-N=N-NH-R' for triazenes, where R, and R' represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. (Not including ortho- chelate substituted aryl azo compounds, and alpha- or beta-substituted alkyl azo compounds.) Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N Valence Stabilizer #14:</u> Formazans, Bis(formazans), and Poly(formazans) without ortho- hydroxy, carboxy, thiol, mercapto, amino, or hydrazido substitution (N-N Bidentates, N-N Tetridentates, and N-N Hexadentates)	R-N=N-CR'=N-NR''R''', where R, R', R'', and R''' represent H, or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. (Not

	including ortho- hydroxy, carboxy, thiol, mercapto, amino, or hydrazido substitution.) Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N Valence Stabilizer #15:</u> Hydramides (N-N Bidentates)	R-CH=N-CHR'-N=CHR'', where R, R', and R'' represent H, or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. (R, R', and R'' are typically aryl derivatives.) Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N Valence Stabilizer #16:</u> Azines (including ketazines), Bis(azines), and Poly(azines) without ortho- hydroxy, carboxy, thiol, mercapto, amino, or hydrazido substitution (N-N Bidentates, N-N Tetridentates, and N-N Hexadentates)	RR'C=N-N=CR''R''' or RR'C=N-NR''R''' (for ketazines), where R, R', R'', and R''' represent H, or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. (Not including ortho- hydroxy, carboxy, thiol, mercapto, amino, or hydrazido substitution.) Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N Valence Stabilizer #17:</u> Schiff Bases with one Imine (C=N) Group and without ortho- (for aryl constituents) or alpha- or beta- (for alkyl constituents) hydroxy, carboxy, carbonyl, thiol, mercapto, thiocarbonyl, amino, imino, oximo, diazeno, or hydrazido substitution (N Monodentates)	RR'C=N-R'', where R, R', and R'' represent H, or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. (Not including ortho-, alpha-, or beta-hydroxy, carboxy, carbonyl, thiol, mercapto, thiocarbonyl, amino, imino, oximo, diazeno, or hydrazido substitution.) Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N Valence Stabilizer #18:</u> Isocyanide and Cyanamide and related ligands (N Monodentates)	Isocyanides, cyanamides, and related ligands where the nitrogen atom is directly complexed to the high valence metal ion.
<u>N Valence Stabilizer #19:</u> Nitrosyl and Nitrite and related ligands (N Monodentates)	Nitrosyl, nitrite, and related ligands where the nitrogen atom is bound directly to the high valence metal ion.
<u>N Valence Stabilizer #20:</u> Nitriles, Dinitriles, and Polynitriles (N Monodentates, N-N Bidentates, and N-N-N Tridentates)	R-CN, R-(CN) ₂ , R-(CN) _x , etc. where R represents H or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>N Valence Stabilizer #21:</u> Azide ligands (N Monodentates, or N-N	Azide (-N ₃) ligands bound directly to the high valence metal ion. Also includes organoazide

Bidentates)	derivatives ($R-N_3$), triazenido compounds ($R-N_3-R'$), phosphonyl azides ($R-PO_2H-N_3$), phosphoryl azides ($O-PO_2H-N_3$), and sulfonyl azides ($R-SO_2-N_3$) where R and R' represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 35, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached
<u>S Valence Stabilizer #1:</u> Monothioethers (S Monodentates) wherein at least one Sulfur Atom is a Binding Site	SH_2 , SHR , SR_2 , where R represents H or any organic functional group wherein the number of carbon atoms ranges from 0 to 35, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, P, O, S, or Se atoms.
<u>S Valence Stabilizer #2:</u> Disulfides (S Monodentates) wherein at least one Sulfur Atom is a Binding Site	$R-S-S-R'$, where R and R' represents H or any organic functional group wherein the number of carbon atoms ranges from 0 to 35, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, P, O, S, or Se atoms.
<u>S Valence Stabilizer #3:</u> Dithioethers (S-S Bidentates) wherein at least one Sulfur Atom is a Binding Site	$R-S-R'-S-R''$, where R , R' , and R'' represents H or any organic functional group wherein the number of carbon atoms ranges from 0 to 35, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, P, O, S, or Se atoms.
<u>S Valence Stabilizer #4:</u> Trithioethers (S-S Bidentates or S-S Tridentates) wherein at least one Sulfur Atom is a Binding Site	$R-S-R'-S-R''-S-R'''$, where R , R' , R'' , and R''' represents H or any organic functional group wherein the number of carbon atoms ranges from 0 to 35, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, P, O, S, or Se atoms.
<u>S Valence Stabilizer #5:</u> Tetrathioethers (S-S Bidentates, S-S Tridentates, or S-S Bidentates) wherein at least one Sulfur Atom is a Binding Site	$R-S-R'-S-R''-S-R'''-S-R''''$, where R , R' , R'' , R''' , and R'''' represents H or any organic functional group wherein the number of carbon atoms ranges from 0 to 35, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, P, O, S, or Se atoms.
<u>S Valence Stabilizer #6:</u>	$R-S-R'-S-R''-S-R'''-S-R''''-S-R'''''-S-R''''''$,

<p>Hexathioethers (S-S Bidentates, S-S Tridentates, S-S Tetridentates, or S-S Hexadentates) wherein at least one Sulfur Atom is a Binding Site</p>	<p>where R, R', R'', R''', R''''', R'''''', and R''''''' represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 35, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, P, O, S, or Se atoms.</p>
<p><u>S Valence Stabilizer #7:</u> Five-Membered Heterocyclic Rings containing One or Two Sulfur Atoms wherein at least one Sulfur Atom is a Binding Site (S Monodentates or S-S Bidentates)</p>	<p>Five membered heterocyclic ring containing one or two sulfur atoms, both of which may function as binding sites. Can include other ring systems bound to this heterocyclic ring, but they do not coordinate with the stabilized, high valence metal ion. Ring can also contain O, N, P, As, or Se atoms. This 5-membered ring and/or attached, uncoordinating rings may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.</p>
<p><u>S Valence Stabilizer #8:</u> Six-Membered Heterocyclic Rings containing One or Two Sulfur Atoms wherein at least one Sulfur Atom is a Binding Site (S Monodentates or S-S Bidentates)</p>	<p>Six membered heterocyclic ring containing just one or two sulfur atoms, both of which may function as binding sites. Can include other ring systems bound to this heterocyclic ring, but they do not coordinate with the stabilized, high valence metal ion. Ring can also contain O, N, P, As, or Se atoms. This 5-membered ring and/or attached, uncoordinating rings may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.</p>
<p><u>S Valence Stabilizer #9:</u> Five-Membered Heterocyclic Rings containing One or Two Sulfur Atoms at least one additional Sulfur Atom Binding Site not in a Ring (S Monodentates, S-S Bidentates, S-S Tridentates, S-S Tetridentates, or S-S Hexadentates)</p>	<p>Five membered heterocyclic ring(s) containing one or two sulfur atoms. In addition, ligand contains additional sulfur-containing substituents (usually thiols or thioethers) that constitute S binding sites. Can include other ring systems bound to the heterocyclic ring or to the S-containing substituent, but they do not coordinate with the stabilized, high valence metal ion. Ring(s) can also contain O, N, P, As or Se atoms. This 5-membered ring(s) and/or attached, uncoordinating rings and/or S-containing substituent(s) may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.</p>
<p><u>S Valence Stabilizer #10:</u> Six-Membered Heterocyclic Rings containing One or Two Sulfur Atoms at least one additional Sulfur Atom Binding Site not in a Ring (S Monodentates, S-S</p>	<p>Six membered heterocyclic ring(s) containing one or two sulfur atoms. In addition, ligand contains additional sulfur-containing substituents (usually thiols or thioethers) that constitute S binding sites. Can include other</p>

Bidentates, S-S Tridentates, S-S Tetridentates, or S-S Hexadentates)	ring systems bound to the heterocyclic ring or to the S-containing substituent, but they do not coordinate with the stabilized, high valence metal ion. Ring(s) can also contain O, N, P, As or Se atoms. This 6-membered ring(s) and/or attached, uncoordinating rings and/or S-containing substituent(s) may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>S Valence Stabilizer #11:</u> Five-Membered Heterocyclic Rings containing One or Two Sulfur Atoms at least one additional Sulfur Atom Binding Site in a separate Ring (S Monodentates, S-S Bidentates, S-S Tridentates, S-S Tetridentates, or S-S Hexadentates)	Five membered heterocyclic ring(s) containing one or two sulfur atoms. In addition, ligand contains additional sulfur-containing rings that constitute S binding sites. Can include other ring systems bound to the S-containing heterocyclic rings, but they do not coordinate with the stabilized, high valence metal ion. Ring(s) can also contain O, N, P, As, or Se atoms. This 5-membered ring(s) and/or additional S-containing ring(s) and/or attached, uncoordinating rings may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>S Valence Stabilizer #12:</u> Six-Membered Heterocyclic Rings containing One or Two Sulfur Atoms at least one additional Sulfur Atom Binding Site in a separate Ring (S Monodentates, S-S Bidentates, S-S Tridentates, S-S Tetridentates, or S-S Hexadentates)	Six membered heterocyclic ring(s) containing one or two sulfur atoms. In addition, ligand contains additional sulfur-containing rings that constitute S binding sites. Can include other ring systems bound to the S-containing heterocyclic rings, but they do not coordinate with the stabilized, high valence metal ion. Ring(s) can also contain O, N, P, As, or Se atoms. This 6-membered ring(s) and/or additional S-containing ring(s) and/or attached, uncoordinating rings may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>S Valence Stabilizer #13:</u> Two-, Three-, Four-, Five-, Six-, Seven-, Eight-, Nine-, and Ten-Membered Macrocyclics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Sulfur (usually thiol or thioether groups) and are not contained in Component Heterocyclic Rings (S-S Bidentates, S-S Tridentates, S-S Tetridentates, and S-S	Macrocyclic ligands containing two to ten sulfur binding sites to valence stabilize the central metal ion. Can include other hydrocarbon or ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbons/rings may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.

Hexadentates)	
S Valence Stabilizer #14: Four-, Five-, Six-, Seven-, Eight-, Nine-, or Ten-Membered Macrocylics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Sulfur and are contained in Component 5-Membered Heterocyclic Rings (S-S Tridentates, S-S Tetridentates or S-S Hexadentates)	Macrocyclic ligands containing a total of four to ten five-membered heterocyclic rings containing sulfur binding sites. Can include other hydrocarbon/ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbon/rings may or may not have halogen or polarizing or water-insolubilizing groups attached.
S Valence Stabilizer #15: Four-, Five-, Six-, Seven-, Eight-, Nine-, or Ten-Membered Macrocylics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Sulfur and are contained in a Combination of 5-Membered Heterocyclic Rings and Thiol, Thioether, or Thioketo Groups (S-S Tridentates, S-S Tetridentates, or S-S Hexadentates)	Macrocyclic ligands containing at least one 5-membered heterocyclic ring. These heterocyclic rings provide sulfur binding sites to stabilize the central metal ion. Other thiol, thioether, or thioketo binding sites can also be included in the macrocyclic ligand, so long as the total number of binding sites is four to ten. Can include other hydrocarbon/ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbon/rings may or may not have halogen or polarizing or water-insolubilizing groups attached.
S Valence Stabilizer #16: Four-, Five-, Six-, Seven-, Eight-, Nine-, or Ten-Membered Macrocylics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Sulfur and are contained in Component 6-Membered Heterocyclic Rings (S-S Tridentates, S-S Tetridentates, or S-S Hexadentates)	Macrocyclic ligands containing a total of four to ten six-membered heterocyclic rings containing sulfur binding sites. Can include other hydrocarbon/ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbon/rings may or may not have halogen or polarizing or water-insolubilizing groups attached.
S Valence Stabilizer #17: Four-, Five-, Six-, Seven-, Eight-, Nine-, or Ten-Membered Macrocylics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Sulfur and are contained in a Combination of 6-Membered Heterocyclic Rings and Thiol, Thioether, or Thioketo Groups (S-S Tridentates, S-S Tetridentates, or S-S	Macrocyclic ligands containing at least one 6-membered heterocyclic ring. These heterocyclic rings provide sulfur binding sites to stabilize the central metal ion. Other thiol, thioether, or thioketo binding sites can also be included in the macrocyclic ligand, so long as the total number of binding sites is four to ten. Can include other hydrocarbon/ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached,

Hexadentates)	uncoordinating hydrocarbon/rings may or may not have halogen or polarizing or water-insolubilizing groups attached.
<u>S Valence Stabilizer #18:</u> Dithiobiurets (Dithioimidodicarbonic Diamides), Dithioisobiurets, Dithiobiureas, Trithiotriurets, Trithiotriureas, Bis(dithiobiurets), Bis(dithioisobiurets), Bis(dithiobiureas), Poly(dithiobiurets), Poly(dithioisobiurets), and Poly(dithiobiureas) (S-S Bidentates, S-S Tridentates, S-S Tetridentates)	RR'-N-C(=S)-NR"-C(=S)-NR'''R"" for dithiobiurets, and RR'-N-C(=S)-NR"-NH-C(=S)-NR""R"" for dithiobiureas, where R, R', R", R"', and R"" represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S Valence Stabilizer #19:</u> Thioacylthioureas, Thioaroylthioureas, Bis(thioacylthioureas), Bis(thioaroylthioureas), Poly(thioacylthioureas), and Poly(thioaroylthioureas) (S-S Bidentates, S-S Tridentates, S-S Tetridentates)	RR'-N-C(=S)-NR"-C(=S)-R"" where R, R', R", and R"" represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S Valence Stabilizer #20:</u> Dithioacyl disulfides, Bis(dithioacyl disulfides), and Poly(dithioacyl disulfides) (S-S Bidentates, S-S Tridentates, S-S Tetridentates)	R-C(=S)-S-S-C(=S)-R' where R, and R' represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S Valence Stabilizer #21:</u> Tetrathioperoxydicarbonic Diamides, Bis(tetrathioperoxydicarbonic diamides), and poly(tetrathioperoxydicarbonic diamides) (S-S Bidentates, S-S Tridentates, S-S Tetridentates)	RR'-N-C(=S)-S-S-C(=S)-N-R"R"" where R, R', R", R"" represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S Valence Stabilizer #22:</u> Hexathio-, Pentathio-, and Tetrathioperoxydicarbonic Acids, Bis(hexathio-, pentathio-, and tetrathioperoxydicarbonic acids), poly(hexathio-, pentathio-, and tetrathioperoxydicarbonic acids), and derivatives thereof (S-S Bidentates, S-S Tridentates, S-S Tetridentates)	R-S-C(=S)-S-S-C(=S)-S-R' for hexathioperoxydicarbonic acids, R-O-C(=S)-S-S-C(=S)-S-R' for pentathioperoxydicarbonic acids, and R-O-C(=S)-S-S-C(=S)-O-R' for tetrathioperoxydicarbonic acids, where R and R' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached.

	Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S Valence Stabilizer #23:</u> Dithioperoxydiphosphoramide, Bis(dithioperoxyphosphoramide), and Poly(dithioperoxydiphosphoramide) (S-S Bidentates, S-S Tridentates, S-S Tetradentates)	(RR'-N-)(R''R'''-N-)P(=S)-S-S-P(=S)(-N-R''''R''''')(-N-R''''''R'''''''), where R, R', R'', R''', R''''', R'''''', and R'''''' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S Valence Stabilizer #24:</u> Dithioperoxydiphosphoric Acids, Bis(dithioperoxyphosphoric Acids), Poly(dithioperoxydiphosphoric Acids), and derivatives thereof (S-S Bidentates, S-S Tridentates, S-S Tetradentates)	(R-O-)(R'-O-)P(=S)-S-S-P(=S)(-O-R'')(-O-R'''); (R-O-)(R'-S-)P(=S)-S-S-P(=S)(-S-R'')(-O-R'''); or (R-S-)(R'-S-)P(=S)-S-S-P(=S)(-S-R'')(-S-R'''), where R, R', R'', R''', R''''', R'''''', and R'''''' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S Valence Stabilizer #25:</u> Dithioimidodiphosphonic Acids, Dithiohydrazidodiphosphonic Acids, Bis(dithioimidodiphosphonic acids), Bis(dithiohydrazidodiphosphonic acids), Poly(dithioimidodiphosphonic acids), Poly(dithiohydrazidodiphosphonic acids), and derivatives thereof (S-S Bidentates, S-S Tridentates, and S-S Tetradentates)	(R-O-)(R'-)P(=S)-NH-P(=S)(-R'')(-O-R'''); (R-S-)(R'-)P(=S)-NH-P(=S)(-R'')(-O-R'''); or (R-S-)(R'-)P(=S)-NH-P(=S)(-R'')(-S-R''') for dithioimidodiphosphonic acids, and -NH-NH-derivatives for dithiohydrazidodiphosphonic acids, where R, R', R'', and R''' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S Valence Stabilizer #26:</u> Dithioimidodiphosphonamides, Dithiohydrazidodiphosphonamides, Bis(dithioimidodiphosphonamides), Bis(dithiohydrazidodiphosphonamides), Poly(dithioimidodiphosphonamides), and Poly(dithiohydrazidodiphosphonamides) (S-S Bidentates, S-S Tridentates, S-S Tetradentates)	(RR'-N-)(R''-)P(=S)-NH-P(=S)(-R''')(-N-R''''R''''') for dithioimidodiphosphonamides, and (RR'-N-)(R''-)P(=S)-NH-NH-P(=S)(-R''')(-N-R''''R''''') for dithiohydrazidodiphosphonamides, where R, R', R'', R''', and R'''' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.

<u>S Valence Stabilizer #27:</u> Dithiodiphosphonamides, Bis(dithiophosphonamides), and Poly(dithiodiphosphonamides) (S-S Bidentates, S-S Tridentates, S-S Tetradentates)	(RR'-N-)(R"-)P(=S)-S-P(=S)(-R'"')(-N-R'"'R'"'), or (RR'-N-)(R"-)P(=S)-O-P(=S)(-R'"')(-N-R'"'R'"'), where R, R', R", R"', R'''', and R'"'' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S Valence Stabilizer #28:</u> Dithiodiphosphonic Acids, Bis(dithioiphosphonic Acids), Poly(dithiodiphosphonic Acids), and derivatives thereof (S-S Bidentates, S-S Tridentates, S-S Tetradentates)	(R-O-)(R'-)P(=S)-O-P(=S)(-R'"')(-O-R'"'); (R-O-)(R'-)P(=S)-S-P(=S)(-R'"')(-O-R'"'); (R-S-)(R'-)P(=S)-O-P(=S)(-R'"')(-S-R'"'); or (R-S-)(R'-)P(=S)-S-P(=S)(-R'"')(-S-R'"'); where R, R', R", and R''' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S Valence Stabilizer #29:</u> Dithioperoxydiphosphonamide, Bis(dithioperoxyphosphonamide), and Poly(dithioperoxydiphosphonamide) (S-S Bidentates, S-S Tridentates, S-S Tetradentates)	(RR'-N-)(R"-)P(=S)-S-S-P(=S)(-R'"')(-N-R'"'R'"'), where R, R', R", R"', R'''', and R'"''' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S Valence Stabilizer #30:</u> Dithioperoxydiphosphonic Acids, Bis(dithioperoxyphosphonic Acids), Poly(dithioperoxydiphosphonic Acids), and derivatives thereof (S-S Bidentates, S-S Tridentates, S-S Tetradentates)	(R-O-)(R'-)P(=S)-S-S-P(=S)(-R'"')(-O-R'"'); or (R-S-)(R'-)P(=S)-S-S-P(=S)(-R'"')(-S-R'"'), where R, R', R", and R''' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S Valence Stabilizer #31:</u> Dithiophosphonic Acids (Phosphonodithioic Acids), Bis(dithiophosphonic Acids), Poly(dithiophosphonic Acids), and derivatives thereof (S-S Bidentates, S-S Tridentates, S-S Tetradentates)	(O=)PR(-S-R')(-S-R") or (S=)PR(-S-R')(-O-R"), where R, R', and R" represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N,

	O, S, or P atoms.
S Valence Stabilizer #32: Trithiophosphonic Acids (Phosphonotriethioic Acids), Bis(trithiophosphonic Acids), Poly(trithiophosphonic Acids), and derivatives thereof (S-S Bidentates, S-S Tridentates, S-S Tetridentates)	(S=)PR(-S-R')(-S-R''), where R, R', and R'' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water- insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
S Valence Stabilizer #33: Phosphono(dithioperoxo)thioic Acids), Bis[phosphono(dithioperoxo)thioic Acids], Poly[phosphono(dithioperoxo)thioic Acids], and derivatives thereof (S-S Bidentates, S-S Tridentates, S-S Tetridentates)	(O=)PR(-S-S-R')(-S-R'') or (S=)PR(-S-S-R')(- O-R''), where R, R', and R'' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
S Valence Stabilizer #34: Phosphono(dithioperoxo)dithioic Acids), Bis[phosphono(dithioperoxo)dithioic Acids], Poly[phosphono(dithioperoxo)dithioic Acids], and derivatives thereof (S-S Bidentates, S-S Tridentates, S-S Tetridentates)	(S=)PR(-S-S-R')(-S-R''), where R, R', and R'' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water- insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
S Valence Stabilizer #35: S-(Alkylthio)thiocarboxylic Acids, S- (Arylthio)thiocarboxylic Acids, and S,S- thiobisthiocarboxylic Acids (S-S Bidentates and S-S Tridentates)	R-S-R'CSOH or R-S-R'CSSH for S- (alkylthio)thiocarboxylic and S- (arylthio)thiocarboxylic acids, and HSOCR-S- R'COSH or HSSCR-S-R'CSSH for S,S- thiobisthiocarboxylic acids, where R and R' represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
S Valence Stabilizer #36: S-(Alkyldisulfido)thiocarboxylic Acids, S- (Aryldisulfido)thiocarboxylic Acids, and S,S'-Disulfidobisthiocarboxylic Acids (S-S Bidentates and S-S Tridentates)	R-S-S-R'CSOH or R-S-S-R'CSSH for S- (alkyldisulfido)thiocarboxylic and S- (aryldisulfido)thiocarboxylic acids, and HSOCR-S-S-R'COSH or HSSCR-S-S-R'CSSH for S,S'-disulfidobisthiocarboxylic acids, where R and R' represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water- insolubilizing/solubilizing groups attached.

	Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S Valence Stabilizer #37:</u> 1,2-Dithiolates, Bis(1,2-dithiolates), and Poly(1,2-dithiolates) (S-S Bidentates, S-S Tridentates, S-S Tetridentates)	R-CH(-SR")-CH(-SR'')-R', and R-C(-SR")=C(-SR'')-R', where R, R', R", and R''' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S Valence Stabilizer #38:</u> Rhodanines and Bis(rhodanines) (S-S Bidentates and S-S Tetridentates)	RN-C(=O)-CHR'-S-C(=S) for rhodanines, and R-[N-C(=O)-CHR'-S-C(=S)] ₂ for bis(rhodanines), where R and R' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S Valence Stabilizer #39:</u> Dithiocarbimates, Bis(dithiocarbimates), and Poly(dithiocarbimates) (S-S Bidentates, S-S Tridentates, and S-S Tetridentates)	RN=C(SH)(SH), where R represents H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S Valence Stabilizer #40:</u> Thioxanthates, Bis(thioxanthates), and Poly(thioxanthates) (S-S Bidentates and S-S Tetridentates)	RS ⁺ =C(SH)(SH) or RS-C(=S)(SH), where R represents H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S Valence Stabilizer #41:</u> Xanthates, Bis(xanthates), and Poly(xanthates) (S-S Bidentates and S-S Tetridentates)	RO ⁺ =C(SH)(SH) or RO-C(=S)(SH), where R represents H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S Valence Stabilizer #42:</u> Phosphinodithioformates (S-S Bidentates)	Typically RR'R''P=C(SH)(SH) [pentavalent P], although RR'P-C(=S)(SH) [trivalent P] may be acceptable in some situations, where R, R', and

	<p>R" represent H, NH₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.</p>
<u>S Valence Stabilizer #43:</u> Alkyl- and Aryl- Dithioborates, Trithioborates, Perthioborates, Bis(dithioborates), Bis(trithioborates), and Bis(perthioborates) (S-S Bidentates and S-S Tetridentates)	R-S-C(-S-R")-O-R' for dithioborates, R-S-C(-S-R")-S-R' for trithioborates, and R-S-S-C(-S-R")-S-R' for perthioborates, where R, R', and R" represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S Valence Stabilizer #44:</u> Alkyl- and Aryl- Dithioboronates, and Bis(dithioboronates) (S-S Bidentates and S-S Tetridentates)	R-C(-S-R")-S-R', where R, R', and R" represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S Valence Stabilizer #45:</u> Trithioarsonic Acids (Arsonotriithioic Acids), Dithioarsonic Acids (Arsonodithioic Acids), Tetraethioarsonic Acids (Arsonotetrathioic Acids), and derivatives thereof (S-S Bidentates, S-S Tridentates, S-S Tetridentates)	(O=)As(-S-R)(-S-R')(-S-R") or (S=)As(-S-R)(-S-R')(-O-R") for trithioarsonic acid; (O=)As(-O-R)(-S-R')(-S-R") or (S=)As(-S-R)(-O-R')(-O-R") for dithioarsonic acid, or (S=)As(-S-R)(-S-R')(-S-R") for tetrathioarsonic acid, where R, R', and R" represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S Valence Stabilizer #46:</u> Trithioantimonic Acids (Stibonotriithioic Acids), Dithioantimonic Acids (Stibonodithioic Acids), Tetraethioantimonic Acids (Stibonotetrathioic Acids), and derivatives thereof (S-S Bidentates, S-S Tridentates, S-S Tetridentates)	(O=)Sb(-S-R)(-S-R')(-S-R") or (S=)Sb(-S-R)(-S-R')(-O-R") for trithioantimonic acid; (O=)Sb(-O-R)(-S-R')(-S-R") or (S=)Sb(-S-R)(-O-R')(-O-R") for dithioantimonic acid, or (S=)Sb(-S-R)(-S-R')(-S-R") for tetrathioantimonic acid, where R, R', and R" represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen

	or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S Valence Stabilizer #47:</u> Phosphine P-sulfides and Amino-substituted Phosphine sulfides (S Monodentates)	RR'R"P=S for phosphine P-sulfides, and (RR'N)(R"R""N)(R'"R""N)P=S for amino-substituted phosphine sulfides, where R, R', R", R'", R"', and R"" represent H, Cl, Br, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. (Rs are typically aromatic or heterocyclic for phosphine P-sulfides.) Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S Valence Stabilizer #48:</u> Arsine As-sulfides and Amino-substituted Arsine sulfides (S Monodentates)	RR'R"As=S for arsine As-sulfides, and (RR'N)(R"R""N)(R'"R""N)As=S for amino-substituted arsine sulfides, where R, R', R", R'", R"', and R"" represent H, Cl, Br, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. (Rs are typically aromatic or heterocyclic for arsine As-sulfides.) Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S Valence Stabilizer #49:</u> Thiolates (S Monodentates)	Thiols (HS-R, HS-R-SH, etc.), where R and R' represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 35, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>S Valence Stabilizer #50:</u> Sulfide ligands (S Monodentates)	Sulfide (-S ²⁻) ligands bound directly to the high valence metal ion.
<u>P Valence Stabilizer #1:</u> Monophosphines (P Monodentates) wherein at least one Phosphorus Atom is a Binding Site	PH ₃ , PH ₂ R, PHR ₂ , and PR ₃ where R represents H or any organic functional group wherein the number of carbon atoms ranges from 0 to 35, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, P, As, O, S, or Se atoms.
<u>P Valence Stabilizer #2:</u> Diphosphines (a P-P Bidentate) wherein at least one Phosphorus Atom is a Binding Site	R'-P-R-P-R", where R, R', and R" represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 35, optionally having halogen or polarizing or

	water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, P, As, O, S, or Se atoms.
<u>P Valence Stabilizer #3:</u> Triphosphines (either P-P Bidentates or P-P Tridentates) wherein at least one Phosphorus Atom is a Binding Site	R-P-R'-P-R"-P-R"', where R, R', R", and R''' represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 35, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, P, As, O, S, or Se atoms.
<u>P Valence Stabilizer #4:</u> Tetraphosphines (P-P Bidentates, P-P Tridentates, or P-P Tetridentates) wherein at least one Phosphorus Atom is a Binding Site	R-P-R'-P-R"-P-R'''-P-R''", where R, R', R", R''' represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 35, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, P, As, O, S, or Se atoms.
<u>P Valence Stabilizer #5:</u> Pentaphosphines (P-P Bidentates, P-P Tridentates, or P-P Tetridentates) wherein at least one Phosphorus Atom is a Binding Site	R-P-R'-P-R"-P-R'''-P-R'''''-P-R''''", where R, R', R", R'''', and R''''' represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 35, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, P, As, O, S, or Se atoms.
<u>P Valence Stabilizer #6:</u> Hexaphosphines (P-P Bidentates, P-P Tridentates, P-P Tetridentates, or P-P Hexadentates) wherein at least one Phosphorus Atom is a Binding Site	R-P-R'-P-R"-P-R'''-P-R'''''-P-R'''''''-P-R''''''", where R, R', R", R'''', R'''''''', and R''''''''' represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 35, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, P, As, O, S, or Se atoms.
<u>P Valence Stabilizer #7:</u> Five-Membered Heterocyclic Rings containing One, Two, or Three Phosphorus Atoms wherein at least one Phosphorus Atom is a Binding Site (P Monodentates or P-P Bidentates)	Five membered heterocyclic ring containing one, two, or three phosphorus atoms, all of which may or may not function as binding sites. Can include other ring systems bound to this heterocyclic ring, but they do not coordinate with the stabilized, high valence metal ion. Ring can also contain O, S, N, As, or Se atoms. This 5-membered ring and/or attached, uncoordinating rings may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>P Valence Stabilizer #8:</u>	Six membered heterocyclic ring containing one,

<p>Six-Membered Heterocyclic Rings containing One, Two, or Three Phosphorus Atoms wherein at least one Phosphorus Atom is a Binding Site (P Monodentates or P-P Bidentates)</p>	<p>two, or three phosphorus atoms, all of which may or may not function as binding sites. Can include other ring systems bound to this heterocyclic ring, but they do not coordinate with the stabilized, high valence metal ion. Ring can also contain O, S, N, As, or Se atoms. This 6-membered ring and/or attached, uncoordinating rings may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.</p>
<p><u>P Valence Stabilizer #9:</u></p> <p>Five-Membered Heterocyclic Rings containing One, Two, or Three Phosphorus Atoms at least one additional Phosphorus Atom Binding Site not in a Ring (P Monodentates, P-P Bidentates, P-P Tridentates, P-P Tetridentates, or P-P Hexadentates)</p>	<p>Five membered heterocyclic ring(s) containing one, two, or three phosphorus atoms. In addition, ligand contains additional phosphorus-containing substituents (usually phosphines) that constitute P binding sites. Can include other ring systems bound to the heterocyclic ring or to the P-containing substituent, but they do not coordinate with the stabilized, high valence metal ion. Ring(s) can also contain O, N, S, As or Se atoms. This 5-membered ring(s) and/or attached, uncoordinating rings and/or P-containing substituent(s) may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.</p>
<p><u>P Valence Stabilizer #10:</u></p> <p>Six-Membered Heterocyclic Rings containing One, Two, or Three Phosphorus Atoms at least one additional Phosphorus Atom Binding Site not in a Ring (P Monodentates, P-P Bidentates, P-P Tridentates, P-P Tetridentates, or P-P Hexadentates)</p>	<p>Six membered heterocyclic ring(s) containing one, two, or three phosphorus atoms. In addition, ligand contains additional phosphorus-containing substituents (usually phosphines) that constitute P binding sites. Can include other ring systems bound to the heterocyclic ring or to the P-containing substituent, but they do not coordinate with the stabilized, high valence metal ion. Ring(s) can also contain O, N, S, As or Se atoms. This 6-membered ring(s) and/or attached, uncoordinating rings and/or P-containing substituent(s) may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.</p>
<p><u>P Valence Stabilizer #11:</u></p> <p>Five-Membered Heterocyclic Rings containing One, Two, or Three Phosphorus Atoms at least one additional Phosphorus Atom Binding Site in a separate Ring (P Monodentates, P-P Bidentates, P-P Tridentates, P-P Tetridentates, or P-P Hexadentates)</p>	<p>Five membered heterocyclic ring(s) containing one, two, or three phosphorus atoms. In addition, ligand contains additional phosphorus-containing rings that constitute P binding sites. Can include other ring systems bound to the P-containing heterocyclic rings, but they do not coordinate with the stabilized, high valence metal ion. Ring(s) can also contain O, N, S, As,</p>

	or Se atoms. This 5-membered ring(s) and/or additional P-containing ring(s) and/or attached, uncoordinating rings may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>P Valence Stabilizer #12:</u> Six-Membered Heterocyclic Rings containing One, Two, or Three Phosphorus Atoms at least one additional Phosphorus Atom Binding Site in a separate Ring (P Monodentates, P-P Bidentates, P-P Tridentates, P-P Tetridentates, or P-P Hexadentates)	Six membered heterocyclic ring(s) containing one, two, or three phosphorus atoms. In addition, ligand contains additional phosphorus-containing rings that constitute P binding sites. Can include other ring systems bound to the P-containing heterocyclic rings, but they do not coordinate with the stabilized, high valence metal ion. Ring(s) can also contain O, N, S, As, or Se atoms. This 6-membered ring(s) and/or additional P-containing ring(s) and/or attached, uncoordinating rings may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>P Valence Stabilizer #13:</u> Two-, Three-, Four-, Five-, Six-, and Eight-Membered Macrocyclics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Phosphorus and are not contained in Component Heterocyclic Rings (P-P Bidentates, P-P Tridentates, P-P Tetridentates, and P-P Hexadentates)	Macrocyclic ligands containing two, three, four, five, six, or eight phosphorus binding sites to valence stabilize the central metal ion. Can include other hydrocarbon or ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbons/rings may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>P Valence Stabilizer #14:</u> Four-, Six-, or Eight-Membered Macrocyclics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Phosphorus and are contained in Component 5-Membered Heterocyclic Rings (P-P Tridentates, P-P Tetridentates, or P-P Hexadentates)	Macrocyclic ligands containing a total of four, six, or eight five-membered heterocyclic rings containing phosphorus binding sites. Can include other hydrocarbon/ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbon/rings may or may not have halogen or polarizing or water-insolubilizing groups attached.
<u>P Valence Stabilizer #15:</u> Four-, Six-, or Eight-Membered Macrocyclics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Phosphorus and are contained in a Combination of 5-Membered Heterocyclic	Macrocyclic ligands containing at least one 5-membered heterocyclic ring. These heterocyclic rings provide phosphorus binding sites to valence stabilize the central metal ion. Other phosphine binding sites can also be included in the macrocyclic ligand, so long as the total number of binding sites is four, six, or eight. Can include other hydrocarbon/ring

Rings and Phosphine Groups (P-P Tridentates, P-P Tetridentates, or P-P Hexadentates)	systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbon/rings may or may not have halogen or polarizing or water-insolubilizing groups attached.
<u>P Valence Stabilizer #16:</u> Four-, Six-, or Eight-Membered Macrocyclics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Phosphorus and are contained in Component 6-Membered Heterocyclic Rings (P-P Tridentates, P-P Tetridentates, or P-P Hexadentates)	Macrocyclic ligands containing a total of four, six, or eight six-membered heterocyclic rings containing phosphorus binding sites. Can include other hydrocarbon/ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbon/rings may or may not have halogen or polarizing or water-insolubilizing groups attached.
<u>P Valence Stabilizer #17:</u> Four-, Six-, or Eight-Membered Macrocyclics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Phosphorus and are contained in a Combination of 6-Membered Heterocyclic Rings and Phosphine Groups (P-P Tridentates, P-P Tetridentates, or P-P Hexadentates)	Macrocyclic ligands containing at least one 6-membered heterocyclic ring. These heterocyclic rings provide phosphorus binding sites to valence stabilize the central metal ion. Other phosphine binding sites can also be included in the macrocyclic ligand, so long as the total number of binding sites is four, six, or eight. Can include other hydrocarbon/ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbon/rings may or may not have halogen or polarizing or water-insolubilizing groups attached.
<u>O Valence Stabilizer #1:</u> Dithioperoxydicarbonic Acids, Bis(dithioperoxydicarbonic acids), poly(dithioperoxydicarbonic acids), and derivatives thereof (O-O Bidentates, O-O Tridentates, O-O Tetridentates)	R-O-C(=O)-S-S-C(=O)-O-R', where R and R' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>O Valence Stabilizer #2:</u> Imidodiphosphonic Acids, Hydrazidodiphosphonic Acids, Bis(imidodiphosphonic Acids), Bis(hydrazidodiphosphonic Acids), Poly(imidodiphosphonic Acids), Poly(hydrazidodiphosphonic Acids), and derivatives thereof (O-O Bidentates, O-O	(R-O-)(R'-)P(=O)-NH-P(=O)(-R'')(-O-R''') for imidodiphosphonic acids, and (R-O-)(R'-)P(=O)-NH-NH-P(=O)(-R'')(-O-R''') for hydrazidodiphosphonic acids; where R, R', R'', and R''' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-

Tridentates, O-O Tetridentates)	insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>O Valence Stabilizer #3:</u> Imidodiphosphonamides, Hydrazidodiphosphonamides, Bis(imidodiphosphonamides), Bis(hydrazidodiphosphonamides), Poly(imidodiphosphonamides), and Poly(hydrazidodiphosphonamides) (O-O Bidentates, O-O Tridentates, O-O Tetridentates)	(RR'-N-)(R"-)P(=O)-NH-P(=O)(-R'"')(-N-R""R""") for imidodiphosphonamides, and –NH-NH- derivatives for hydrazidodiphosphonamides, where R, R', R", R"', R""", and R"""" represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>O Valence Stabilizer #4:</u> Diphosphonamides, Bis(diphosphonamides), and Poly(diphosphonamides) (O-O Bidentates, O-O Tridentates, O-O Tetridentates)	(RR'-N-)(R"-)P(=O)-O-P(=O)(-R'"')(-N-R""R"""), where R, R', R", R"', R""", and R"""" represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>O Valence Stabilizer #5:</u> Carbazates (carbazides), Bis(carbazates), and Poly(carbazates) (O-O Bidentates, O-O Tridentates, and O-O Tetridentates; or possibly N-O Bidentates, N-O Tridentates, and N-O Tetridentates)	RR'N-NR"-C(=O)(OH), where R and R' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>O Valence Stabilizer #6:</u> Arsonic Acids, Bis(arsonic acids), Poly(arsonic acids), and derivatives thereof (O-O Bidentates, O-O Tridentates, O-O Tetridentates)	(O=)As(-O-R)(-O-R')(O-R''), where R, R', and R'' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>O Valence Stabilizer #7:</u> Alkyl- and Aryl- Borates and Bis(borates) (O-O Bidentates and O-O Tetridentates)	R-O-C(-O-R")-O-R', where R, R', and R'' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.

	P atoms.
<u>O Valence Stabilizer #8:</u> Alkyl- and Aryl- Boronates and Bis(boronates) (O-O Bidentates and O-O Tetradentates)	R-C(-O-R")-O-R', where R, R', and R" represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>O Valence Stabilizer #9:</u> Phosphine P-oxides and Amino-substituted Phosphine oxides (O Monodentates)	RR'R"P=O for phosphine P-oxides, and (RR'N)(R"R'"N)(R""R""N)P=O for amino-substituted phosphine oxides, where R, R', R", R'", R""", and R"""" represent H, Cl, Br, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. (Rs are typically aromatic or heterocyclic for phosphine P-oxides.) Ligand can also contain nonbinding N, O, S, or P atoms.
<u>O Valence Stabilizer #10:</u> Arsine As-oxides and Amino-substituted Arsine oxides (O Monodentates)	RR'R"As=O for arsine As-oxides, and (RR'N)(R"R'"N)(R""R""N)As=O for amino-substituted arsine oxides, where R, R', R", R'", R""", and R"""" represent H, Cl, Br, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. (Rs are typically aromatic or heterocyclic for arsine As-oxides.) Ligand can also contain nonbinding N, O, S, or P atoms.
<u>O Valence Stabilizer #11:</u> Five-Membered Heterocyclic Rings containing One or Two Oxygen Atoms wherein at least one Oxygen Atom is a Binding Site (O Monodentates or O-O Bidentates)	Five membered heterocyclic ring containing one or two oxygen atoms, both of which may or may not function as binding sites. Can include other ring systems bound to this heterocyclic ring, but they do not coordinate with the stabilized, high valence metal ion. Ring can also contain O, S, or P atoms. This 5-membered ring and/or attached, uncoordinating rings may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>O Valence Stabilizer #12:</u> Six-Membered Heterocyclic Rings containing One or Two Oxygen Atoms wherein at least one Oxygen Atom is a	Six membered heterocyclic ring containing one or two oxygen atoms, both of which may or may not function as binding sites. Can include other ring systems bound to this heterocyclic

Binding Site (O Monodentates or O-O Bidentates)	ring, but they do not coordinate with the stabilized, high valence metal ion. Ring can also contain O, S, or P atoms. This 6-membered ring and/or attached, uncoordinating rings may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>O Valence Stabilizer #13:</u> Five-Membered Heterocyclic Rings containing One or Two Oxygen Atoms and having at least one additional Oxygen Atom Binding Site not in a Ring (O Monodentates, O-O Bidentates, O Tridentates, O Tetridentates, or O Hexadentates)	Five membered heterocyclic ring(s) containing one or two oxygen atoms. In addition, ligand contains additional oxygen-containing substituents (usually hydroxyl or ester groups) that constitute O binding sites. Can include other ring systems bound to the heterocyclic ring or to the O-containing substituent, but they do not coordinate with the stabilized, high valence metal ion. Ring(s) can also contain O, S, or P atoms. This 5-membered ring(s) and/or attached, uncoordinating rings and/or O-containing substituent(s) may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>O Valence Stabilizer #14:</u> Six-Membered Heterocyclic Rings containing One or Two Oxygen Atoms and having at least one additional Oxygen Atom Binding Site not in a Ring (O Monodentates, O-O Bidentates, O Tridentates, O Tetridentates, or O Hexadentates)	Six membered heterocyclic ring(s) containing one or two oxygen atoms. In addition, ligand contains additional oxygen-containing substituents (usually hydroxyl or ester groups) that constitute O binding sites. Can include other ring systems bound to the heterocyclic ring or to the O-containing substituent, but they do not coordinate with the stabilized, high valence metal ion. Ring(s) can also contain O, S, or P atoms. This 6-membered ring(s) and/or attached, uncoordinating rings and/or O-containing substituent(s) may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>O Valence Stabilizer #15:</u> Five-Membered Heterocyclic Rings containing One or Two Oxygen Atoms and having at least one additional Oxygen Atom Binding Site in a Separate Ring (O Monodentates, O-O Bidentates, O Tridentates, O Tetridentates, or O Hexadentates)	Five membered heterocyclic ring(s) containing one or two oxygen atoms. In addition, ligand contains additional oxygen-containing rings that constitute O binding sites. Can include other ring systems bound to the O-containing heterocyclic rings, but they do not coordinate with the stabilized, high valence metal ion. Ring(s) can also contain O, S, or P atoms. This 5-membered ring(s) and/or additional O-containing ring(s) and/or attached, uncoordinating rings may or may not have halogen or polarizing or water-

	insolubilizing/solubilizing groups attached.
<u>O Valence Stabilizer #16:</u> Six-Membered Heterocyclic Rings containing One or Two Oxygen Atoms and having at least one additional Oxygen Atom Binding Site in a Separate Ring (O Monodentates, O-O Bidentates, O Tridentates, O Tetridentates, or O Hexadentates)	Six membered heterocyclic ring(s) containing one or two oxygen atoms. In addition, ligand contains additional oxygen-containing rings that constitute O binding sites. Can include other ring systems bound to the O-containing heterocyclic rings, but they do not coordinate with the stabilized, high valence metal ion. Ring(s) can also contain O, S, or P atoms. This 6-membered ring(s) and/or additional O-containing ring(s) and/or attached, uncoordinating rings may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>O Valence Stabilizer #17:</u> Four-, Five-, Six-, Seven-, Eight-, and Ten-Membered Macrocyclics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Oxygen (usually ester or hydroxyl groups) and are not contained in Component Heterocyclic Rings (O-O Bidentates, O-O Tridentates, O-O Tetridentates, and O-O Hexadentates)	Macrocyclic ligands containing four, five, six, seven, eight, or ten oxygen binding sites to valence stabilize the central metal ion. Can include other hydrocarbon or ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbons/rings may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>O Valence Stabilizer #18:</u> Four-, Five-, Six-, Seven-, Eight-, and Ten-Membered Macrocyclics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Oxygen and are contained in Component 5-Membered Heterocyclic Rings (O-O Bidentates, O-O Tridentates, O-O Tetridentates, and O-O Hexadentates)	Macrocyclic ligands containing a total of four, five, six, seven, eight, or ten five-membered heterocyclic rings containing oxygen binding sites. Can include other hydrocarbon or ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbons/rings may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>O Valence Stabilizer #19:</u> Four-, Five-, Six-, Seven-, Eight-, and Ten-Membered Macrocyclics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Oxygen and are contained in Component 6-Membered Heterocyclic Rings (O-O Bidentates, O-O Tridentates, O-O Tetridentates, and O-O Hexadentates)	Macrocyclic ligands containing a total of four, five, six, seven, eight, or ten six-membered heterocyclic rings containing oxygen binding sites. Can include other hydrocarbon or ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbons/rings may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>N-S Valence Stabilizer #1:</u>	RC(=NH)SR', where R and R' represent H or

<p>Thioimidates, Dithioimidates, Polythioimidates, and Derivatives of Thioimidic Acid (N-S Bidentates and N-S Tetridentates)</p>	<p>any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.</p>
<p>N-S Valence Stabilizer #2: Thioguanylureas, Guanidinothioureas, Bis(thioguanylureas), Bis(guanidinothioureas), Poly(thioguanylureas), and Poly(guanidinothioureas) (N-S Bidentates and N-S Tetridentates)</p>	<p>RR'-N-C(=NH)-NR"-CS-NR'''R"" for thioguanylureas, and RR'-N-C(=NH)-NR"-NH-CS-NR'''R"" for guanidinothioureas, where R, R', R'', and R''' represent H, NH₂, or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.</p>
<p>N-S Valence Stabilizer #3: Amidinothioamides, Guanidinothioamides, Bis(amidinothioamides), Bis(guanidinothioamides), Poly(amidinothioamides), and Poly(guanidinothioamides) (including both N-amidinothioamides and 2-amidinothioacetamides) (N-S Bidentates and N-S Tetridentates)</p>	<p>RR'-N-C(=NH)-NR"-CS-R"" for N-amidinothioamides, or RR'-N-C(=NH)-CR'R"-CS-N-R'''R"" for 2-amidinothioacetamides, and RR'-N-C(=NH)-NR"-NH-CS-R"" for guanidinothioamides, where R, R', R'', R''', R'''', and R''''' represent H, NH₂, or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.</p>
<p>N-S Valence Stabilizer #4: Imidoylthioamides, Bis(imidoylthioamides), and Poly(imidoylthioamides) (N-S Bidentates and N-S Tetridentates)</p>	<p>R-C(=NH)-NR'-CS-R'', where R, R', and R'', represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.</p>
<p>N-S Valence Stabilizer #5: Thioureas, Bis(thioureas), and Poly(thioureas), including Thiourylene Complexes (N-S Bidentates, N-S Tridentates, and N-S Tetridentates)</p>	<p>RR'NCSNR''R''', where R, R', R'', and R''' represent H, NH₂, or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.</p>
<p>N-S Valence Stabilizer #6: Thiocarboxamides, Bis(thiocarboxamides), and Poly(thiocarboxamides) (N-S</p>	<p>RCSNR'R'', where R, R', and R'' represent H, NH₂, or any organic functional group wherein the number of carbon atoms ranges from 0 to</p>

Bidentates, N-S Tridentates, and N-S Tetridentates)	40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-S Valence Stabilizer #7:</u> Imidosulfurous Diamides and Bis(imidosulfurous diamides) (N-S Bidentates, N-S Tridentates, and N-S Tetridentates)	RR'-N-S(=NH)-N-R''R''', where R, R', R'', and R''' represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-S Valence Stabilizer #8:</u> Sulfurdiimines, Bis(sulfurdiimines), and Poly(sulfurdiimines) (N-S Bidentates, N-S Tridentates, and N-S Tetridentates)	R-N=S=N-R', where R and R' represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-S Valence Stabilizer #9:</u> Phosphonimidothioic Acid, Phosphonimidodithioic Acid, Bis(Phosphonimidothioic acid); Bis(Phosphonimidodithioic acid), and derivatives thereof (N-S Bidentates, N-S Tetridentates)	(NH=)PR(OR')(SR') for phosphonimidothioic acid and (NH=)PR(SR')(SR') for phosphonimidodithioic acid, where R, R', and R'' represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-S Valence Stabilizer #10:</u> Phosphonothioic Diamides, Bis(phosphonothioic diamides), and Poly(phosphonothioic diamides) (N-S Bidentates and N-S Tetridentates)	(S=)PR(-NR'R'')(-NR'''R'''), where R, R', R'', R''', and R''' represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-S Valence Stabilizer #11:</u> Phosphonamidothioic Acid, Phosphonamidimidodithioic Acid, Bis(phosphonamidothioic acid), Bis(phosphonamidimidodithioic acid), poly(phosphonamidothioic acid), and poly(phosphonamidimidodithioic acid), and derivatives thereof (N-S Bidentates and N-S Tetridentates)	(S=)PR(-NR'R'')(-OR''') or (O=)PR(-NR'R'')(-SR''') for phosphonamidothioic acid, (S=)PR(-NR'R'')(-SR''') for phosphonamidimidodithioic acid, where R, R', R'', and R''' represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-S Valence Stabilizer #12:</u>	R-C(=S)-CR'=CR''-NHR''', where R, R', R'',

Beta-Aminothiones (N-Substituted 3-amino-2-propenethioaldehydes), Bis(beta-aminothiones), and Poly(beta-aminothiones) (N-S Bidentates and N-S Tetridentates)	and R''' represent H, or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
N-S Valence Stabilizer #13: 3-Aminothioacrylamides (3-Amino-2-thiopropenamides), 3,3-Diaminothioacrylamides, Bis(3-aminothioacrylamides), Bis(3,3-diaminoacrylamides), Poly(3-aminothioacrylamides), and Poly(3,3-diaminothioacrylamides) (N-S Bidentates and N-S Tetridentates)	RR'-N-C(=S)-CR'=C(-NHR''')R''' for 3-aminothioacrylamides, and RR'-N-C(=S)-CR'=C(-NHR''')(NR''''R''''') for 3,3-diaminothioacrylamides, where R, R', R'', R''', R'''' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
N-S Valence Stabilizer #14: 3-Aminothioacrylic Acids (3-Amino-2-thiopropenoic acids), 3-Mercapto-3-aminothioacrylic acids, Bis(3-aminothioacrylic acids), Bis(3-Hydroxy-3-aminothioacrylic acids), Poly(3-aminothioacrylic acids), and Poly(3-Hydroxy-3-aminothioacrylic acids), and derivatives thereof (N-S Bidentates and N-S Tetridentates)	R-O-C(=S)-CR'=C(-NHR''')R''' or R-S-C(=S)-CR'=C(-NHR''')R''' for 3-aminothioacrylic acids, and R-O-C(=S)-CR'=C(-NHR'')(-S-R''') or R-S-C(=S)-CR'=C(-NHR'')(-S-R''') for 3-mercапто-3-aminothioacrylic acids, where R, R', R'', and R''' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
N-S Valence Stabilizer #15: N-Thioacyl Benzylidenimines, Bis(N-thioacyl benzylidenimines), and Poly(N-thioacyl benzylidenimines) (N-S Bidentates and N-S Tetridentates)	R-C(=S)-N=CHR', where R' represents an aromatic derivative (i.e., -C ₆ H ₅), and R represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
N-S Valence Stabilizer #16: Thiocarbonyl oximes, Bis(thiocarbonyl oximes), and Poly(thiocarbonyl oximes) (N-S Bidentates, N-S Tridentates, and N-S Tetridentates)	R-C(=S)-C(=NOH)-R', where R and R' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or

	P atoms.
N-S Valence Stabilizer #17: Mercapto oximes, Bis(mercaptop oximes), and Poly(mercaptop oximes) (including 2-sulfur heterocyclic oximes) (N-S Bidentates, N-S Tridentates, N-S Tetridentates, and N-S Hexadentates)	R-CH(-SH)-C(=NOH)-R', where R, R', and R'' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
N-S Valence Stabilizer #18: 2-Nitrothiophenols (2-nitrobenzenethiols) (N-S Bidentates)	o-(O ₂ N-)(HS-)Ar, where Ar represents an aromatic group or heterocyclic wherein the number of carbon atoms ranges from 6 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
N-S Valence Stabilizer #19: 2-Nitrilo thiophenols (N-S Bidentates)	o-(NC-(CH ₂) ₀₋₁)(HS-)Ar, where Ar represents an aromatic group or heterocyclic wherein the number of carbon atoms ranges from 6 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
N-S Valence Stabilizer #20: Thiohydrazides, Bis(thiohydrazides), and Poly(thiohydrazides) (N-S Bidentates and N-S Tetridentates)	R-C(=S)-NHNR'R'', where R, R', and R'' represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
N-S Valence Stabilizer #21: Thiosemicarbazides, Bis(thiosemicarbazides), and Poly(thiosemicarbazides) (N-S Bidentates, N-S Tetridentates, and N-S Hexadentates)	RR'-N-C(=S)-NHNR''R''', where R, R', and R''' represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
N-S Valence Stabilizer #22: Five-, Seven-, or Nine-Membered Macrocyclics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Nitrogen (usually amine or imine groups) or Sulfur (usually thiols, mercaptans, or thiocarbonyls) and are not contained in	Macrocyclic ligands containing five, seven, or nine binding sites composed of nitrogen and sulfur to valence stabilize the central metal ion. Can include other hydrocarbon or ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbons/rings may or may not have halogen or polarizing or water-

Component Heterocyclic Rings (N-S Tridentates, N-S Tetridentates, and N-S Hexadentates)	insolubilizing/solubilizing groups attached.
<u>N-S Valence Stabilizer #23:</u> Five-, or Seven-Membered Macrocylics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Nitrogen or Sulfur and are contained in Component Heterocyclic Rings (N-S Tridentates, N-S Tetridentates, or N-S Hexadentates)	Macrocyclic ligands containing a total of five or seven heterocyclic rings containing nitrogen or sulfur binding sites. Can include other hydrocarbon/ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbon/rings may or may not have halogen or polarizing or water-insolubilizing groups attached.
<u>N-S Valence Stabilizer #24:</u> Five-, Seven-, or Nine-Membered Macrocylics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Nitrogen or Sulfur and are contained in a Combination of Heterocyclic Rings and Amine, Imine, Thiol, Mercapto, or Thiocarbonyl Groups (N-S Tridentates, N-S Tetridentates, or N-S Hexadentates)	Macrocyclic ligands containing at least one heterocyclic ring. These heterocyclic rings provide nitrogen or sulfur binding sites to stabilize the central metal ion. Other amine, imine, thiol, mercapto, or thiocarbonyl binding sites can also be included in the macrocyclic ligand, so long as the total number of binding sites is five, seven, or nine. Can include other hydrocarbon/ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbon/rings may or may not have halogen or polarizing or water-insolubilizing groups attached.
<u>N-O Valence Stabilizer #1:</u> Imidates, Diimidates, Polyimidates, and Derivatives of Imidic Acid (N-O Bidentates and N-O Tetridentates)	$\text{RC}(\text{=NH})\text{OR}'$, where R and R' represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #2:</u> Pseudoureas, bis(pseudoureas), and poly(pseudoureas) (N-O Bidentates and N-O Tetridentates)	$\text{RR}'\text{NC}(\text{=NH})\text{OR}''$, where R, R', and R'' represent H, NH_2 , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #3:</u> 2-Amidinoacetates, Bis(2-amidinoacetates), and Poly(2-amidinoacetates) (N-O	$\text{RR}'\text{NC}(\text{=NH})\text{CR}''\text{R}'''(\text{CO})\text{OR}''''$, where R, R', R'', R''', and R'''' represent H, NH_2 , or any organic functional group wherein the number of

Bidentates and N-O Tetridentates)	carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #4:</u> Ureas, Bis(ureas), and Poly(ureas), including Urylene Complexes (N-O Bidentates, N-O Tridentates, and N-O Tetridentates)	RR'NCONR''R''', where R, R', R'', and R''' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #5:</u> Phosphonimidic Acid, Bis(phosphonimidic acid), Poly(phosphonimidic acid), and derivatives thereof (N-O Bidentates and N-O Tetridentates)	(NH=)PR(OR')(OR'''), where R, R', and R'' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #6:</u> Phosphonamidic Acid, Phosphonic Diamide, Bis(Phosphonamidic Acid), Bis(Phosphonic Diamide), Poly(phosphonamidic acid), poly(phosphonic diamide), and derivatives thereof (N-O Bidentates and N-O Tetridentates)	(O=)PR(-NR'R'')(-OR''') for phosphonamidic acid and (O=)PR(-NR'R'')(-NR'''R''''') for phosphonic diamide, where R, R', R'', R''', and R'''' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #7:</u> Beta-Ketoamines (N-Substituted 3-amino-2-propenals), Bis(beta-ketoamines), and Poly(beta-ketoamines) (N-O Bidentates and N-O Tetridentates)	R-C(=O)-CR'=C(-NHR'')R''', where R, R', R'', and R''' represent H, or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #8:</u> 3-Aminoacrylamides (3-Amino-2-propenamides), 3,3-Diaminoacrylamides, Bis(3-aminoacrylamides), Bis(3,3-diaminoacrylamides), Poly(3-aminoacrylamides), and Poly(3,3-diaminoacrylamides) (N-O Bidentates and	RR'-N-C(=O)-CR''=C(-NHR''')R'''' for 3-aminoacrylamides, and RR'-N-C(=O)-CR''=C(-NHR''')(-NR''''R''''') for 3,3-diaminoacrylamides, where R, R', R'', R''', R''''', and R''''' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having

N-O Tetridentates)	halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #9:</u> 3-Aminoacrylic Acids (3-Amino-2-propenoic acids), 3-Hydroxy-3-aminoacrylic acids, Bis(3-aminoacrylic acids), Bis(3-Hydroxy-3-aminoacrylic acids), Poly(3-aminoacrylic acids), and Poly(3-Hydroxy-3-aminoacrylic acids), and derivatives thereof (N-O Bidentates and N-O Tetridentates)	R-O-C(=O)-CR' = C(-NHR")R''' for 3-aminoacrylic acids, and R-O-C(=O)-CR' = C(-NHR")(-O-R''') for 3-hydroxy-3-aminoacrylic acids, where R, R', R'', and R''' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #10:</u> N-Acyl Benzylidenimines, Bis(N-acyl benzylidenimines), and Poly(N-acyl benzylidenimines) (N-O Bidentates and N-O Tetridentates)	R-C(=O)-N=CHR', where R' represents an aromatic derivative (i.e., -C ₆ H ₅), and R represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #11:</u> 2-Nitroanilines (N-O Bidentates)	o-(O ₂ N-)(RR'N-)Ar, where Ar represents an aromatic group or heterocyclic wherein the number of carbon atoms ranges from 6 to 40, and R and R' represent H, NH ₂ , or alkyl or aryl hydrocarbon groups wherein the number of carbon atoms range from 0 to 25, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #12:</u> 2-Nitrilophenols (N-O Bidentates). Also includes acylcyanamides.	o-(NC-(CH ₂) ₀₋₁)(HO-)Ar, where Ar represents an aromatic group or heterocyclic wherein the number of carbon atoms ranges from 6 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #13:</u> Amine N-Oxides and Diazine N-Oxides (Azoxy compounds) (N-O Bidentates, N-O Tridentates, and N-O Tetridentates)	HetN ⁺ -O ⁻ for amine N-oxides, and R-N=N ⁺ (-O ⁻)R' for diazine N-oxides (azoxy compounds), where Het represents a nitrogen-containing heterocyclic derivative wherein the number of carbon atoms ranges from 4 to 40, and R and R' represent separate or the same aromatic

	functionalities, both Het and R,R' optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #14:</u> Hydrazides, Bis(hydrazides), and Poly(hydrazides) (N-O Bidentates and N-O Tetridentates)	R-C(=O)-NHNR'R'', where R, R', and R'' represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #15:</u> Semicarbazides, Bis(semicarbazides), and Poly(semicarbazides) (N-O Bidentates, N-O Tetridentates, and N-O Hexadentates)	RR'-N-C(=O)-NHNR''R''', where R, R', and R''' represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>N-O Valence Stabilizer #16:</u> Five-, Seven-, or Nine-Membered Macrocyclics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Nitrogen (usually amine or imine groups) or Oxygen (usually hydroxy, carboxy, or carbonyl groups) and are not contained in Component Heterocyclic Rings (N-O Tridentates, N-O Tetridentates, and N-O Hexadentates)	Macrocyclic ligands containing five, seven, or nine binding sites composed of nitrogen and oxygen to valence stabilize the central metal ion. Can include other hydrocarbon or ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbons/rings may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>N-O Valence Stabilizer #17:</u> Five-, or Seven-Membered Macrocyclics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Nitrogen or Oxygen and are contained in Component Heterocyclic Rings (N-O Tridentates, N-O Tetridentates, or N-O Hexadentates)	Macrocyclic ligands containing a total of five or seven heterocyclic rings containing nitrogen or oxygen binding sites. Can include other hydrocarbon/ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbon/rings may or may not have halogen or polarizing or water-insolubilizing groups attached.
<u>N-O Valence Stabilizer #18:</u> Five-, Seven-, or Nine-Membered Macrocyclics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates)	Macrocyclic ligands containing at least one heterocyclic ring. These heterocyclic rings provide nitrogen or oxygen binding sites to valence stabilize the central metal ion. Other amine, imine, hydroxy, carboxy, or carbonyl

<p>wherein all Binding Sites are composed of Nitrogen or Oxygen and are contained in a Combination of Heterocyclic Rings and Amine, Imine, Hydroxy, Carboxy, or Carbonyl Groups (N-O Tridentates, N-O Tetridentates, or N-O Hexadentates)</p>	<p>binding sites can also be included in the macrocyclic ligand, so long as the total number of binding sites is five, seven, or nine. Can include other hydrocarbon/ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbon/rings may or may not have halogen or polarizing or water-insolubilizing groups attached.</p>
<p><u>S-O Valence Stabilizer #1:</u> Thiobiurets (Thioimidodicarbonic Diamides), Thioisobiurets, Thiobiureas, Thiotriurets, Thiotriureas, Bis(thiobiurets), Bis(thioisobiurets), Bis(thiobiureas), Poly(thiobiurets), Poly(thioisobiurets), Poly(thiobiureas) (S-O Bidentates, S-O Tridentates, S-O Tetridentates), and 3-formamidino thiocarbamides</p>	<p>$RR'-N-C(=S)-NR''-C(=O)-NR'''R''''$ for thiobiurets, and $RR'-N-C(=S)-NR''-NH-C(=O)-NR'''R''''$ for thiobiureas, where R, R', R'', R''', and R'''' represent H, NH₂, or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.</p>
<p><u>S-O Valence Stabilizer #2:</u> Acylthioureas, Aroylthioureas, Thioacylureas, Thioaroylureas, Bis(acylthioureas), Bis(aroylthioureas), Bis(thioacylureas), Bis(thioaroylureas), Poly(thioacylthioureas), Poly(thioaroylthioureas), Poly(thioacylureas), and Poly(thioaroylureas) (S-O Bidentates, S-O Tridentates, S-O Tetridentates)</p>	<p>$RR'-N-C(=S)-NR''-C(=O)-R''''$ for acyl- and aroylthioureas, and $RR'-N-C(=O)-NR''-C(=S)-R''''$ for thioacyl- and thioaroylureas, where R, R', R'', and R'''' represent H, NH₂, or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.</p>
<p><u>S-O Valence Stabilizer #3:</u> Thioimidodialdehydes, Thiohydrazidodialdehydes (thioacyl hydrazides), Bis(thioimidodialdehydes), Bis(thiohydrazidodialdehydes), Poly(thioimidodialdehydes), and Poly(thiohydrazidodialdehydes) (S-O Bidentates, S-O Tridentates, S-O Tetridentates)</p>	<p>$RC(=S)-NR'-C(=O)-R''$ for thioimidodialdehydes, and $RC(=S)-NR'-NH-C(=O)-R''$ for thiohydrazidodialdehydes (thioacyl hydrazides), where R, R', and R'' represent H, NH₂, or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.</p>
<p><u>S-O Valence Stabilizer #4:</u> Thioimidodicarbonic acids, Thiohydrazidodicarbonic acids, Bis(thioimidodicarbonic acids), Bis(thiohydrazidodicarbonic acids),</p>	<p>$R-O-C(=S)-NR'-C(=O)-O-R''$ or $R-S-C(=S)-NR'-C(=O)-S-R''$ for thioimidodicarbonic acids, and $R-O-C(=S)-NR'-NH-C(=O)-O-R''$ or $R-S-C(=S)-NR'-NH-C(=O)-S-R''$ for thiohydrazidodicarbonic acids, where R, R', and</p>

Poly(thioimidodicarbonic acids), Poly(thiohydrazidodicarbonic acids) and derivatives thereof (S-O Bidentates, S-O Tridentates, S-O Tetridentates)	R" represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S-O Valence Stabilizer #5:</u> 1,2-Monothioketones (Monothiolenes, Monothio-alpha-ketonates), 1,2,3-Monothioketones, 1,2,3-Dithioketones, Monothiotropolonates, ortho-Monothioquinones, Bis(1,2-Monothioketones), and Poly(1,2-Monothioketones) (S-O Bidentates, S-O Tridentates, S-O Tetridentates)	R-C(=S)-C(=O)-R' where R and R' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S-O Valence Stabilizer #6:</u> Trithioperoxydicarbonic Diamides, Dithioperoxydicarbonic Diamides, Bis(trithioperoxydicarbonic diamides), Bis(dithioperoxydicarbonic diamides), poly(trithioperoxydicarbonic diamides) and poly(dithioperoxydicarbonic diamides) (S-O Bidentates, S-O Tridentates, S-O Tetridentates)	RR'-N-C(=S)-S-S-C(=O)-N-R"R''' for trithioperoxydicarbonic diamides, and RR'-N-C(=O)-S-S-C(=O)-N-R"R''' for dithioperoxydicarbonic diamides, where R, R', R", R''' represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S-O Valence Stabilizer #7:</u> Diithiodicarbonic Acids, Bis(dithiodicarbonic acids), Poly(dithiodicarbonic acids), and derivatives thereof (S-O Bidentates, S-O Tridentates, S-O Tetridentates)	R-O-C(=S)-S-C(=O)-O-R', where R and R' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S-O Valence Stabilizer #8:</u> Trithioperoxydicarbonic Acids, Bis(trithioperoxydicarbonic acids), poly(trithioperoxydicarbonic acids), and derivatives thereof (S-O Bidentates, S-O Tridentates, S-O Tetridentates)	R-O-C(=S)-S-S-C(=O)-O-R', where R and R' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S-O Valence Stabilizer #9:</u> Monothioperoxydiphosphoramido, Bis(monothioperoxyphosphoramido), and	(RR'-N-)(R"R'''-N-)P(=S)-S-S-P(=O)(-N-R""R''')(-N-R''''R'''''), where R, R', R", R'', R''', R''''', R''''''', and R''''''' represent H, NH ₂ or

Poly(monothioperoxydiphosphoramido) (S-O Bidentates, S-O Tridentates, S-O Tetridentates)	any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S-O Valence Stabilizer #10:</u> Monothioperoxydiphosphoric Acids, Bis(monothioperoxyphosphoric Acids), Poly(monothioperoxydiphosphoric Acids), and derivatives thereof (S-O Bidentates, S-O Tridentates, S-O Tetridentates)	(R-O-)(R'-O-)P(=S)-S-S-P(=O)(-O-R'')(-O-R'''); (R-O-)(R'-S-)P(=S)-S-S-P(=O)(-S-R'')(-O-R'''); or (R-S-)(R'-S-)P(=S)-S-S-P(=O)(-S-R'')(-S-R'''), where R, R', R'', R''', R'''', R''''', and R''''' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S-O Valence Stabilizer #11:</u> Monothioimidodiphosphonic Acids, Monothiohydrazidodiphosphonic Acids, Bis(monothioimidodiphosphonic Acids), Bis(monothiohydrazidodiphosphonic Acids), Poly(monothioimidodiphosphonic Acid), Poly(monothiohydrazidodiphosphonic Acids), and derivatives thereof (S-O Bidentates, S-O Tridentates, S-O Tetridentates)	(R-O-)(R'-)P(=S)-NH-P(=O)(-R'')(-O-R'''); (R-S-)(R'-)P(=S)-NH-P(=O)(-R'')(-O-R'''); or (R-S-)(R'-)P(=S)-NH-P(=O)(-R'')(-S-R''') for monothioimidodiphosphonic acids, and -NH-NH- derivatives for monothiohydrazidodiphosphonic acids, where R, R', R'', and R''' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S-O Valence Stabilizer #12:</u> Monothioimidodiphosphonamides, Monothiohydrazidodiphosphonamides, Bis(monothioimidodiphosphonamides), Bis(monothiohydrazidodiphosphonamides) Poly(monothioimidodiphosphonamides), and Poly(monothiohydrazidodiphosphonamides) (S-O Bidentates, S-O Tridentates, S-O Tetridentates)	(RR'-N-)(R''-)P(=S)-NH-P(=O)(-R'')(-N-R''''R''''') for monothioimidodiphosphonamides, and -NH-NH- derivatives for monothiohydrazidodiphosphonamides, where R, R', R'', R''', and R''''' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S-O Valence Stabilizer #13:</u> Monothiodiphosphonamides, Bis(monothiophosphonamides), and Poly(monothiodiphosphonamides) (S-O Bidentates, S-O Tridentates, S-O	(RR'-N-)(R''-)P(=S)-S-P(=O)(-R'')(-N-R''''R'''''), or (RR'-N-)(R''-)P(=S)-O-P(=O)(-R'')(-N-R''''R'''''), where R, R', R'', R''', R'''', and R''''' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.

Tetradentates)	atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
S-O Valence Stabilizer #14: Monothiodiphosphonic Acids, Bis(monothioiphosphonic Acids), Poly(monothiodiphosphonic Acids), and derivatives thereof (S-O Bidentates, S-O Tridentates, S-O Tetradentates)	(R-O-)(R'-)P(=S)-O-P(=O)(-R'')(-O-R'''); (R-O-)(R'-)P(=S)-S-P(=O)(-R'')(-O-R'''); (R-S-)(R'-)P(=S)-O-P(=O)(-R'')(-S-R'''); or (R-S-)(R'-)P(=S)-S-P(=O)(-R'')(-S-R'''), where R, R', R'', and R''' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
S-O Valence Stabilizer #15: Monothioperoxydiphosphonamide, Bis(monothioperoxyphosphonamide), and Poly(monothioperoxydiphosphonamide) (S-O Bidentates, S-O Tridentates, S-O Tetradentates)	(RR'-N-)(R''-)P(=S)-S-S-P(=O)(-R''')(-N-R''''R'''''), where R, R', R'', R''', R''''', and R''''' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
S-O Valence Stabilizer #16: Monothioperoxydiphosphonic Acids, Bis(monothioperoxyphosphonic Acids), Poly(monothioperoxydiphosphonic Acids), and derivatives thereof (S-O Bidentates, S-O Tridentates, S-O Tetradentates)	(R-O-)(R'-)P(=S)-S-S-P(=O)(-R'')(-O-R'''); or (R-S-)(R'-)P(=S)-S-S-P(=O)(-R'')(-S-R'''), where R, R', R'', and R''' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
S-O Valence Stabilizer #17: Monothiophosphoric Acids (Phosphorothioic Acids), Bis(monothiophosphoric acids), Poly(monothiophosphoric acids), and derivatives thereof (S-O Bidentates, S-O Tridentates, S-O Tetradentates)	(O=P(-S-R)(-O-R'))(-O-R'') or (S=P(-O-R)(-O-R'))(-O-R''), where R, R', and R'' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
S-O Valence Stabilizer #18: Phosphoro(dithioperoxoic) Acids, Bis[phosphoro(dithioperoxoic) acids], Poly[phosphoro(dithioperoxoic) acids], and	(O=P(-S-S-R)(-O-R'))(-O-R''), where R, R', and R'' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having

derivatives thereof (S-O Bidentates, S-O Tridentates, S-O Tetradentates)	halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S-O Valence Stabilizer #19:</u> Monothiophosphonic Acids (Phosphonothioic Acids), Bis(monothiophosphonic Acids), Poly(monothiophosphonic Acids), and derivatives thereof (S-O Bidentates, S-O Tridentates, S-O Tetradentates)	(O=)PR(-S-R')(-O-R'') or (S=)PR(-O-R')(-O-R''), where R, R', and R'' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S-O Valence Stabilizer #20:</u> Phosphono(dithioperoxoic) Acids, Bis[phosphono(dithioperoxoic) Acids], Poly[phosphono(dithioperoxoic) Acids], and derivatives thereof (S-O Bidentates, S-O Tridentates, S-O Tetradentates)	(O=)PR(-S-S-R')(-O-R''), where R, R', and R'' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S-O Valence Stabilizer #21:</u> Beta-Hydroxythioketones, Beta-Hydroxythioaldehydes, Bis(beta-hydroxythioketones), Bis(beta-hydroxythioaldehydes), Poly(beta-hydroxythioketones), and Poly(beta-hydroxythioaldehydes) (S-O Bidentates, S-O Tridentates, S-O Tetradentates)	R-CR'(-OH)-CH ₂ -C(=S)-R'', where R, R', and R'' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S-O Valence Stabilizer #22:</u> Beta-Mercaptoketones, Beta-Mercaptoaldehydes, Bis(beta-mercaptoketones), Bis(beta-mercaptopaldehydes), Poly(beta-mercaptoketones), and Poly(beta-mercaptopaldehydes) (S-O Bidentates, S-O Tridentates, S-O Tetradentates)	R-CR'(-SH)-CH ₂ -C(=O)-R'', where R, R', and R'' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S-O Valence Stabilizer #23:</u> N-(Aminomethylol)thioureas [N-(Aminohydroxymethyl)thioureas], Bis[N-(aminomethylol)thioureas], and Poly[N-(aminomethylol)thioureas] (S-O Bidentates, S-O Tridentates, S-O Tetradentates)	RR'-N-CH(-OH)-NR''-C(=S)-NR'''R'''', where R, R', R'', R''', and R'''' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S-O Valence Stabilizer #24:</u> N-(Aminomethylthiol)ureas [N-	RR'-N-CH(-SH)-NR''-C(=O)-NR'''R'''', where R, R', R'', R''', and R'''' represent H, NH ₂ or any

(Aminomercaptomethyl)ureas], Bis[N-(aminomethylthiol)ureas], and Poly[N-(aminomethylthiol)ureas] (S-O Bidentates, S-O Tridentates, S-O Tetridentates)	organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S-O Valence Stabilizer #25:</u> Monothiooxamides, Bis(monothiooxamides), and Poly(monothiooxamides) (S-O Bidentates, S-O Tridentates, S-O Tetridentates)	RR'-N-C(=S)-C(=O)-N-R''R'''', where R, R', R'', and R''' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S-O Valence Stabilizer #26:</u> Beta-Mercapto Carboxylic Acids, Bis(Beta-Mercapto Carboxylic Acids), Poly(Beta-Mercapto Carboxylic Acids), and derivatives thereof (S-O Bidentates, S-O Tridentates, S-O Tetridentates)	R-CR'(-SH)-CR''R'''-C(=O)(-O-R'''''), where R, R', R'', R''', and R''''' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S-O Valence Stabilizer #27:</u> Beta-Mercapto Thiocarboxylic Acids, Bis(Beta-Mercapto Thiocarboxylic Acids), Poly(Beta-Mercapto Thiocarboxylic Acids), and derivatives thereof (S-O Bidentates, S-O Tridentates, S-O Tetridentates)	R-CR'(-SH)-CR''R'''-C(=O)(-S-R'''''), where R, R', R'', R''', and R''''' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S-O Valence Stabilizer #28:</u> Beta-Hydroxy Thiocarboxylic Acids, Bis(Beta-Hydroxy Thiocarboxylic Acids), Poly(Beta-Hydroxy Thiocarboxylic Acids), and derivatives thereof (S-O Bidentates, S-O Tridentates, S-O Tetridentates)	R-CR'(-OH)-CR''R'''-C(=O)(-S-R'''''), where R, R', R'', R''', and R''''' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S-O Valence Stabilizer #29:</u> Beta-Mercapto Carboxamides, Bis(Beta-Mercapto Carboxamides), Poly(Beta-Mercapto Carboxamides), and derivatives thereof (S-O Bidentates, S-O Tridentates, S-O Tetridentates)	R-CR'(-SH)-CR''R'''-C(=O)(-NH-R'''''), where R, R', R'', R''', and R''''' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.

<u>S-O Valence Stabilizer #30:</u> S-Alkylthiocarboxylic Acids, S-Arylthiocarboxylic Acids, and S,S-thiobiscarboxylic Acids (S-O Bidentates and S-O Tridentates)	R-S-R'COOH for S-alkylthiocarboxylic and S-arylthiocarboxylic acids, and HOOCR-S-R'COOH for S,S-thiobiscarboxylic acids, where R and R' represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S-O Valence Stabilizer #31:</u> S-Alkyldisulfidocarboxylic Acids, S-Aryldisulfidocarboxylic Acids, and S,S'-Disulfidobiscarboxylic Acids (S-O Bidentates and S-O Tridentates)	R-S-S-R'COOH for S-alkyldisulfidocarboxylic and S-aryldisulfidocarboxylic acids, and HOOCR-S-S-R'COOH for S,S'-disulfidobiscarboxylic acids, where R and R' represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S-O Valence Stabilizer #32:</u> Monothiomonocarboxylic Acids, Dithiodicarboxylic Acids, Bis(monothiomonocarboxylic Acids), Bis(dithiodicarboxylic acids), Poly(monothiomonocarboxylic acids), Poly(dithiodicarboxylic acids), and derivatives thereof (S-O Bidentates and S-O Tetridentates)	R-C(=O)(-S-R') for monothiomonocarboxylic acids, and (R-S-)(O=)C-R'-C(=O)(-S-R") or (R-S-)(O=)C-R'-C(=O)(-O-R") for dithiodicarboxylic acids, where R, R', and R" represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S-O Valence Stabilizer #33:</u> Monothiocarbonates and Bis(monothiocarbonates) (S-O Bidentates and S-O Tetridentates)	R-O-C(=S)-O-R', where R, and R' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S-O Valence Stabilizer #34:</u> Monothiocarbazates (Monothiocarbazides), Bis(monothiocarbazates), and Poly(monothiocarbazates) (S-O Bidentates, S-O Tridentates, and S-O Tetridentates; or possibly N-S Bidentates, N-S Tridentates, and N-S Tetridentates)	RR'N-NR"-C(=O)(SH), where R and R' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.

<u>S-O Valence Stabilizer #35:</u> Mercapto Alcohols and Silylmercaptoalcohols, Bis(mercaptopo alcohols and silylmercaptoalcohols), and Poly(mercaptopo alcohols and silylmercaptoalcohols) (S-O Bidentates, S-O Tridentates, S-O Tetridentates)	R-CH(-SH)-CH(-OH)-R' for alpha-mercaptopo alcohols, R-CH(-SH)-Si(-OR') _x -R" _{3-x} for alpha-silylmercaptoalcohols, R-CH(-SH)-R'-CH(-OH)-R" for beta-mercaptopo alcohols, and R-CH(-SH)-R'-Si(-OR") _x -R" _{3-x} for beta-silylmercaptoalcohols, etc., where R, R', R", and R" represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. x = 1-3. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S-O Valence Stabilizer #36:</u> Monothiocarbimates, Bis(monothiocarbimates), and Poly(monothiocarbimates) (S-O Bidentates, S-O Tridentates, and S-O Tetridentates)	RN=C(OH)(SH), where R represents H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S-O Valence Stabilizer #37:</u> Alkyl- and Aryl- Monothioborates and Bis(monothioborates) (S-O Bidentates and S-O Tetridentates)	R-O-C(-S-R")-O-R', where R, R', and R" represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S-O Valence Stabilizer #38:</u> Alkyl- and Aryl- Monothioboronates and Bis(monothioboronates) (S-O Bidentates and S-O Tetridentates)	R-C(-S-R")-O-R', where R, R', and R" represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S-O Valence Stabilizer #39:</u> Monothioarsonic Acids (Arsonothioic Acids), Bis(monothioarsonic acids), Poly(monothioarsonic acids), and derivatives thereof (S-O Bidentates, S-O Tridentates, S-O Tetridentates)	(O=)As(-S-R)(-O-R')(-O-R") or (S=)As(-O-R)(-O-R')(-O-R"), where R, R', and R" represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>S-O Valence Stabilizer #40:</u>	Heterocyclic ring(s) containing one or two

<p>Heterocyclic Rings containing One or Two Sulfur Atoms at least one additional Oxygen Atom Binding Site not in a Ring (S-O Bidentates, S-O Tridentates, S-O Tetridentates, or S-O Hexadentates)</p>	<p>sulfur atoms. In addition, ligand contains additional oxygen-containing substituents (usually hydroxy, carboxy, or carbonyl groups) that constitute O binding sites. Can include other ring systems bound to the heterocyclic ring or to the O-containing substituent, but they do not coordinate with the stabilized, high valence metal ion. Ring(s) can also contain O, N, P, As or Se atoms. This 5-membered ring(s) and/or attached, uncoordinating rings and/or O-containing substituent(s) may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.</p>
<p><u>S-O Valence Stabilizer #41:</u> Heterocyclic Rings containing One or Two Oxygen Atoms at least one additional Sulfur Atom Binding Site not in a Ring (S-O Bidentates, S-O Tridentates, S-O Tetridentates, or S-O Hexadentates)</p>	<p>Heterocyclic ring(s) containing one or two oxygen atoms. In addition, ligand contains additional sulfur-containing substituents (usually thio, mercapto, or thiocarbonyl groups) that constitute S binding sites. Can include other ring systems bound to the heterocyclic ring or to the S-containing substituent, but they do not coordinate with the stabilized, high valence metal ion. Ring(s) can also contain O, N, P, As or Se atoms. This 5-membered ring(s) and/or attached, uncoordinating rings and/or S-containing substituent(s) may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.</p>
<p><u>S-O Valence Stabilizer #42:</u> Heterocyclic Rings containing One or Two Sulfur Atoms at least one additional Oxygen Atom Binding Site in a separate Ring (S-O Bidentates, S-O Tridentates, S-O Tetridentates, or S-O Hexadentates)</p>	<p>Heterocyclic ring(s) containing one or two sulfur atoms. In addition, ligand contains additional oxygen-containing rings that constitute O binding sites. Can include other ring systems bound to the O-containing heterocyclic rings, but they do not coordinate with the stabilized, high valence metal ion. Ring(s) can also contain O, N, P, As, or Se atoms. This 5-membered ring(s) and/or additional O-containing ring(s) and/or attached, uncoordinating rings may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.</p>
<p><u>S-O Valence Stabilizer #43:</u> Two-, Three-, Four-, Five-, Six-, Seven-, Eight-, Nine-, and Ten-Membered Macrocyclics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates)</p>	<p>Macrocylic ligands containing two to ten sulfur or oxygen binding sites to valence stabilize the central metal ion. Can include other hydrocarbon or ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This</p>

<p>wherein all Binding Sites are composed of Sulfur (usually thiol, mercapto, or thiocarbonyl groups) or Oxygen (hydroxy, carboxy, or carbonyl groups) and are not contained in Component Heterocyclic Rings (S-O Bidentates, S-O Tridentates, S-O Tetridentates, and S-O Hexadentates)</p>	<p>ligand and/or attached, uncoordinating hydrocarbons/rings may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.</p>
<p><u>S-O Valence Stabilizer #44:</u> Four-, Five-, Six-, Seven-, Eight-, Nine-, or Ten-Membered Macrocyclics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Sulfur or Oxygen and are contained in Component 5-Membered Heterocyclic Rings (S-O Tridentates, S-O Tetridentates or S-O Hexadentates)</p>	<p>Macrocylic ligands containing a total of four to ten five-membered heterocyclic rings containing sulfur or oxygen binding sites. Can include other hydrocarbon/ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbon/rings may or may not have halogen or polarizing or water-insolubilizing groups attached.</p>
<p><u>S-O Valence Stabilizer #45:</u> Four-, Five-, Six-, Seven-, Eight-, Nine-, or Ten-Membered Macrocyclics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Sulfur or Oxygen and are contained in a Combination of Heterocyclic Rings and Thiol, Mercapto, Thiocarbonyl, Hydroxy, Carboxy, and Carbonyl Groups (S-O Tridentates, S-O Tetridentates, or S-O Hexadentates)</p>	<p>Macrocylic ligands containing at least one heterocyclic ring. These heterocyclic rings provide sulfur or oxygen binding sites to valence stabilize the central metal ion. Other thiol, mercapto, thiocarbonyl, hydroxy, carboxy, or carbonyl binding sites can also be included in the macrocyclic ligand, so long as the total number of binding sites is four to ten. Can include other hydrocarbon/ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbon/rings may or may not have halogen or polarizing or water-insolubilizing groups attached.</p>
<p><u>S-O Valence Stabilizer #46:</u> Sulfoxides (S-O Bidentates)</p>	<p>Sulfoxides ($R-SO-R'$), where R and R' represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 35, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached.</p>
<p><u>S-O Valence Stabilizer #47:</u> Sulfones (S-O Bidentates)</p>	<p>Sulfones ($R-SO_2-R'$), where R and R' represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 35, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached.</p>
<p><u>S-O Valence Stabilizer #48:</u></p>	<p>Sulfur dioxide ligands ($-SO_2$) bound directly to</p>

Sulfur dioxide (SO_2) ligands (S-O Bidentates)	the high valence metal ion.
<u>N-P Valence Stabilizer #1:</u> Aminoaryl Phosphines and Iminoaryl Phosphines (N-P Bidentates, N-P Tridentates, and N-P Tetridentates)	[R(-NR'R'')(-PR'''R''')] _x , [R(-NR'R'') _x] ₁₋₃ P, [R(-NR'R'') _x] ₁₋₃ PX, or [R(-PR'R'') _x] ₁₋₃ N, where X = O or S and R, R', R'', R''', and R'''' represents H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 35, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, P, O, S, or Se atoms.
<u>N-P Valence Stabilizer #2:</u> Heterocyclic Rings containing One, Two, Three, or Four Nitrogen Atoms at least one additional Phosphorus Atom Binding Site not in a Ring (N-P Bidentates, N-P Tridentates, N-P Tetridentates, or N-P Hexadentates)	Five membered heterocyclic ring(s) containing one, two, three, or four nitrogen atoms. In addition, ligand contains additional phosphorus-containing substituents that constitute P binding sites. Can include other ring systems bound to the heterocyclic ring or to the P-containing substituent, but they do not coordinate with the stabilized, high valence metal ion. Ring(s) can also contain O, S, or P atoms. This ring(s) and/or attached, uncoordinating rings and/or P-containing substituent(s) may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>N-P Valence Stabilizer #3:</u> Heterocyclic Rings containing One, Two, or Three Phosphorus Atoms at least one additional Nitrogen Atom Binding Site not in a Ring (N-P Bidentates, N-P Tridentates, N-P Tetridentates, or N-P Hexadentates)	Five membered heterocyclic ring(s) containing one, two, or three phosphorus atoms. In addition, ligand contains additional nitrogen-containing substituents (usually amines, imines, or hydrazides) that constitute N binding sites. Can include other ring systems bound to the heterocyclic ring or to the N-containing substituent, but they do not coordinate with the stabilized, high valence metal ion. Ring(s) can also contain O, S, or P atoms. This ring(s) and/or attached, uncoordinating rings and/or N-containing substituent(s) may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>N-P Valence Stabilizer #4:</u> Heterocyclic Rings containing One, Two, Three, or Four Nitrogen Atoms at least one additional Phosphorus Atom Binding Site in a Separate Ring (N-P Bidentates, N-P Tridentates, N-P Tetridentates)	Heterocyclic ring(s) containing one, two, three, or four nitrogen atoms. In addition, ligand contains additional phosphorus-containing rings that constitute P binding sites. Can include other ring systems bound to the N- or P-containing heterocyclic rings, but they do not coordinate with the stabilized, high valence metal ion. Ring(s) can also contain O, S, or P atoms.

	atoms. This ring(s) and/or additional P-containing ring(s) and/or attached, uncoordinating rings may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>N-P Valence Stabilizer #5:</u> Two-, Three-, Four-, Five-, Six-, Seven-, Eight-, Nine-, and Ten-Membered Macrocyclics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Nitrogen (usually amine or imine groups) or Phosphorus and are not contained in Component Heterocyclic Rings (N-P Bidentates, N-P Tridentates, N-P Tetridentates, and N-P Hexadentates)	Macrocyclic ligands containing two, three, four, five, six, seven, eight, nine, or ten binding sites composed of nitrogen and phosphorus to valence stabilize the central metal ion. Can include other hydrocarbon or ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbons/rings may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>N-P Valence Stabilizer #6:</u> Four-, Five-, Six-, Seven-, Eight-, Nine-, or Ten-Membered Macrocyclics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Nitrogen or Phosphorus and are contained in Component Heterocyclic Rings (N-P Bidentates, N-P Tridentates, N-P Tetridentates, or N-P Hexadentates)	Macrocyclic ligands containing a total of four, five, six, seven, eight, nine, or ten heterocyclic rings containing nitrogen or phosphorus binding sites. Can include other hydrocarbon/ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbon/rings may or may not have halogen or polarizing or water-insolubilizing groups attached.
<u>N-P Valence Stabilizer #7:</u> Four-, Five-, Six-, Seven-, Eight-, Nine-, or Ten-Membered Macrocyclics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Nitrogen or Phosphorus and are contained in a Combination of Heterocyclic Rings and Amine, Imine, and Phosphine Groups (N-P Bidentates, N-P Tridentates, N-P Tetridentates, or N-P Hexadentates)	Macrocyclic ligands containing at least one heterocyclic ring. These heterocyclic rings provide nitrogen or phosphorus binding sites to valence stabilize the central metal ion. Other amine, imine, or phosphine binding sites can also be included in the macrocyclic ligand, so long as the total number of binding sites is four, five, six, seven, eight, nine, or ten. Can include other hydrocarbon/ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbon/rings may or may not have halogen or polarizing or water-insolubilizing groups attached.
<u>S-P Valence Stabilizer #1:</u> Thioaryl Phosphines (S-P Bidentates, S-P Tridentates, and S-P Tetridentates)	[R(-SR') _x] ₁₋₃ P, [R(-SR') _x] ₁₋₃ PX, [R(-PR'R'')(-SR'')] _x , [R(-PR'R'')(-S-S-R'')] _x , [R(-PR'R'')(-C(=S)R'')] _x , [R(-PR'R'') _x] ₂ S, [R(-PR'R'') _x] ₂

	$\text{R}^{\prime\prime\prime}(-\text{SR}^{\prime\prime\prime})_y, [\text{R}(-\text{SR}')_x]_{2-3}\text{R}^{\prime\prime}(-\text{PR}^{\prime\prime\prime}\text{R}^{\prime\prime\prime})_y, [\text{R}(-\text{PR}'\text{R}')_x]_2\text{S}_2,$ and $[\text{R}(-\text{PR}'\text{R}')_x]_2\text{R}^{\prime\prime\prime}(\text{C}(=\text{S}))_y\text{R}^{\prime\prime\prime},$ where X = O or S, and R, R', R'', R''', and R'''' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached, and x = 1-2 and y = 1-4. Ligand can also contain nonbinding N, O, S, or P atoms.
S-P Valence Stabilizer #2: Heterocyclic Rings containing One or Two Sulfur Atoms at least one additional Phosphorus Atom Binding Site not in a Ring (P-S Bidentates, P-S Tridentates, P-S Tetridentates, or P-S Hexadentates)	Heterocyclic ring(s) containing one or two sulfur atoms. In addition, ligand contains additional phosphorus-containing substituents that constitute P binding sites. Can include other ring systems bound to the heterocyclic ring or to the P-containing substituent, but they do not coordinate with the stabilized, high valence metal ion. Ring(s) can also contain O, S, or P atoms. This ring(s) and/or attached, uncoordinating rings and/or P-containing substituent(s) may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
S-P Valence Stabilizer #3: Heterocyclic Rings containing One, Two, or Three Phosphorus Atoms at least one additional Sulfur Atom Binding Site not in a Ring (S-P Bidentates, S-P Tridentates, S-P Tetridentates, or S-P Hexadentates)	Heterocyclic ring(s) containing one, two, or three phosphorus atoms. In addition, ligand contains additional sulfur-containing substituents (usually thiol, mercapto, or thiocarbonyl groups) that constitute S binding sites. Can include other ring systems bound to the heterocyclic ring or to the S-containing substituent, but they do not coordinate with the stabilized, high valence metal ion. Ring(s) can also contain O, S, or P atoms. This ring(s) and/or attached, uncoordinating rings and/or S-containing substituent(s) may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
S-P Valence Stabilizer #4: Heterocyclic Rings containing One or Two Sulfur Atoms at least one additional Phosphorus Atom Binding Site in a Separate Ring (S-P Bidentates, S-P Tridentates, S-P Tetridentates)	Heterocyclic ring(s) containing one or two sulfur atoms. In addition, ligand contains additional phosphorus-containing rings that constitute P binding sites. Can include other ring systems bound to the S- or P-containing heterocyclic rings, but they do not coordinate with the stabilized, high valence metal ion. Ring(s) can also contain O, S, or P atoms. This ring(s) and/or additional P-containing ring(s)

	and/or attached, uncoordinating rings may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>S-P Valence Stabilizer #5:</u> Two-, Three-, Four-, Five-, Six-, Seven-, Eight-, Nine-, and Ten-Membered Macrocyclics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Sulfur (usually thiol, mercapto, or thiocarbonyl groups) or Phosphorus and are not contained in Component Heterocyclic Rings (S-P Bidentates, S-P Tridentates, S-P Tetridentates, and S-P Hexadentates)	Macrocylic ligands containing two, three, four, five, six, seven, eight, nine, or ten binding sites composed of sulfur and phosphorus to valence stabilize the central metal ion. Can include other hydrocarbon or ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbons/rings may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>S-P Valence Stabilizer #6:</u> Four-, Five-, Six-, Seven-, Eight-, Nine-, or Ten-Membered Macrocyclics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Sulfur or Phosphorus and are contained in Component Heterocyclic Rings (S-P Bidentates, S-P Tridentates, S-P Tetridentates, or S-P Hexadentates)	Macrocylic ligands containing a total of four, five, six, seven, eight, nine, or ten heterocyclic rings containing sulfur or phosphorus binding sites. Can include other hydrocarbon/ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbon/rings may or may not have halogen or polarizing or water-insolubilizing groups attached.
<u>S-P Valence Stabilizer #7:</u> Four-, Five-, Six-, Seven-, Eight-, Nine-, or Ten-Membered Macrocyclics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Sulfur or Phosphorus and are contained in a Combination of Heterocyclic Rings and Thiol, Mercapto, Thiocarbonyl or Phosphine Groups (S-P Bidentates, S-P Tridentates, S-P Tetridentates, or S-P Hexadentates)	Macrocylic ligands containing at least one heterocyclic ring. These heterocyclic rings provide sulfur or phosphorus binding sites to valence stabilize the central metal ion. Other thiol, mercapto, or thiocarbonyl, or phosphine binding sites can also be included in the macrocyclic ligand, so long as the total number of binding sites is four, five, six, seven, eight, nine, or ten. Can include other hydrocarbon/ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbon/rings may or may not have halogen or polarizing or water-insolubilizing groups attached.
<u>P-O Valence Stabilizer #1:</u> Hydroxyaryl Phosphines (P-O Bidentates, P-O Tridentates, and P-O Tetridentates)	[R(-OR') _x] ₁₋₃ P, [R(-OR') _x] ₁₋₃ PX, [R(-PR'R")(-OR'')], [R(-PR'R")(-C(=O)R'')], [R(-PR'R") _x] ₂ O, [R(-PR'R") _x] ₂₋₃ R'"(-OR'') _y , [R(-OR') _x] ₂₋₃ R'"(-PR'"R'') _y , and [R(-

	$\text{PR}'\text{R}''\text{x}_2\text{R}'''(\text{C}(=\text{O}))_y\text{R}''''$, where X = O or S, and R, R', R'', R''', and R'''' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached, and x = 1-2 and y = 1-4. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>P-O Valence Stabilizer #2:</u> Heterocyclic Rings containing One or Two Oxygen Atoms at least one additional Phosphorus Atom Binding Site not in a Ring (P-O Bidentates, P-O Tridentates, P-O Tetridentates, or P-O Hexadentates)	Heterocyclic ring(s) containing one or two oxygen atoms. In addition, ligand contains additional phosphorus-containing substituents that constitute P binding sites. Can include other ring systems bound to the heterocyclic ring or to the P-containing substituent, but they do not coordinate with the stabilized, high valence metal ion. Ring(s) can also contain O, S, or P atoms. This ring(s) and/or attached, uncoordinating rings and/or P-containing substituent(s) may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>P-O Valence Stabilizer #3:</u> Heterocyclic Rings containing One, Two, or Three Phosphorus Atoms at least one additional Oxygen Atom Binding Site not in a Ring (P-O Bidentates, P-O Tridentates, P-O Tetridentates, or P-O Hexadentates)	Heterocyclic ring(s) containing one, two, or three phosphorus atoms. In addition, ligand contains additional oxygen-containing substituents (usually hydroxy, carboxy, or carbonyl groups) that constitute O binding sites. Can include other ring systems bound to the heterocyclic ring or to the O-containing substituent, but they do not coordinate with the stabilized, high valence metal ion. Ring(s) can also contain O, S, or P atoms. This ring(s) and/or attached, uncoordinating rings and/or O-containing substituent(s) may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>P-O Valence Stabilizer #4:</u> Heterocyclic Rings containing One or Two Oxygen Atoms at least one additional Phosphorus Atom Binding Site in a Separate Ring (P-O Bidentates, P-O Tridentates, P-O Tetridentates)	Heterocyclic ring(s) containing one or two oxygen atoms. In addition, ligand contains additional phosphorus-containing rings that constitute P binding sites. Can include other ring systems bound to the O- or P-containing heterocyclic rings, but they do not coordinate with the stabilized, high valence metal ion. Ring(s) can also contain O, S, or P atoms. This ring(s) and/or additional P-containing ring(s) and/or attached, uncoordinating rings may or may not have halogen or polarizing or water-

	insolubilizing/solubilizing groups attached.
<u>P-O Valence Stabilizer #5:</u> Two-, Three-, Four-, Five-, Six-, Seven-, Eight-, Nine-, and Ten-Membered Macrocyclics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Oxygen (usually hydroxy, carboxy, or carbonyl groups) or Phosphorus and are not contained in Component Heterocyclic Rings (P-O Bidentates, P-O Tridentates, P-O Tetridentates, and P-O Hexadentates)	Macrocyclic ligands containing two, three, four, five, six, seven, eight, nine, or ten binding sites composed of oxygen and phosphorus to valence stabilize the central metal ion. Can include other hydrocarbon or ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbons/rings may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>P-O Valence Stabilizer #6:</u> Four-, Five-, Six-, Seven-, Eight-, Nine-, or Ten-Membered Macrocyclics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Oxygen or Phosphorus and are contained in Component Heterocyclic Rings (P-O Bidentates, P-O Tridentates, P-O Tetridentates, or P-O Hexadentates)	Macrocyclic ligands containing a total of four, five, six, seven, eight, nine, or ten heterocyclic rings containing oxygen or phosphorus binding sites. Can include other hydrocarbon/ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbon/rings may or may not have halogen or polarizing or water-insolubilizing groups attached.
<u>P-O Valence Stabilizer #7:</u> Four-, Five-, Six-, Seven-, Eight-, Nine-, or Ten-Membered Macrocyclics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Oxygen or Phosphorus and are contained in a Combination of Heterocyclic Rings and Hydroxy, Carboxy, Carbonyl or Phosphine Groups (P-O Bidentates, P-O Tridentates, P-O Tetridentates, or P-O Hexadentates)	Macrocyclic ligands containing at least one heterocyclic ring. These heterocyclic rings provide oxygen or phosphorus binding sites to valence stabilize the central metal ion. Other hydroxy, carboxy, carbonyl, or phosphine binding sites can also be included in the macrocyclic ligand, so long as the total number of binding sites is four, five, six, seven, eight, nine, or ten. Can include other hydrocarbon/ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbon/rings may or may not have halogen or polarizing or water-insolubilizing groups attached.
<u>As Valence Stabilizer #1:</u> Monoarsines (As Monodentates) wherein at least one Arsenic Atom is a Binding Site	AsH ₃ , AsH ₂ R, AsHR ₂ , where R represents H or any organic functional group wherein the number of carbon atoms ranges from 0 to 25, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N,

	P, As, O, S, or Se atoms.
<u>As Valence Stabilizer #2:</u> Diarsines (an As-As Bidentate) wherein at least one Arsenic Atom is a Binding Site	R'-As-R-As-R'', where R, R', and R'' represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 25, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, P, As, O, S, or Se atoms.
<u>As Valence Stabilizer #3:</u> Triarsines (either As-As Bidentates or As-As Tridentates) wherein at least one Arsenic Atom is a Binding Site	R-As-R'-As-R''-As-R''', where R, R', R'', and R''' represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 25, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, P, As, O, S, or Se atoms.
<u>As Valence Stabilizer #4:</u> Tetraarsines (As-As Bidentates, As-As Tridentates, or As-As Tetridentates) wherein at least one Arsenic Atom is a Binding Site	R-As-R'-As-R''-As-R'''-As-R''''', where R, R', R'', R''', and R''''' represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 25, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, P, As, O, S, or Se atoms.
<u>As Valence Stabilizer #5:</u> Pentaarsines (As-As Bidentates, As-As Tridentates, or As-As Tetridentates) wherein at least one Arsenic Atom is a Binding Site	R-As-R'-As-R''-As-R'''-As-R''''-As-R''''', where R, R', R'', R''', R''''', and R''''' represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 25, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, P, As, O, S, or Se atoms.
<u>As Valence Stabilizer #6:</u> Hexaarsines (As-As Bidentates, As-As Tridentates, As-As Tetridentates, or As-As Hexadentates) wherein at least one Arsenic Atom is a Binding Site	R-As-R'-As-R''-As-R'''-As-R''''-As-R''''', where R, R', R'', R''', R''''', and R''''''' represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 25, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, P, As, O, S, or Se atoms.
<u>As Valence Stabilizer #7:</u> Five-Membered Heterocyclic Rings containing One Arsenic Atom wherein the Arsenic Atom is the Binding Site (As Monodentates)	Five membered heterocyclic ring containing just one arsenic binding site. Can include other ring systems bound to this heterocyclic ring, but they do not coordinate with the stabilized, high valence metal ion. Ring can also contain O, S, N, P, or Se atoms. This 5-membered ring

	and/or attached, uncoordinating rings may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>As Valence Stabilizer #8:</u> Six-Membered Heterocyclic Rings containing One Arsenic Atom wherein the Arsenic Atom is the Binding Site (As Monodentates)	Six membered heterocyclic ring containing just one arsenic binding site. Can include other ring systems bound to this heterocyclic ring, but they do not coordinate with the stabilized, high valence metal ion. Ring can also contain O, S, N, P, or Se atoms. This 6-membered ring and/or attached, uncoordinating rings may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>As Valence Stabilizer #9:</u> Five-Membered Heterocyclic Rings containing One Arsenic Atom and having at least one additional Arsenic Atom Binding Site not in a Ring (As Monodentates, As-As Bidentates, As-As Tridentates, As-As Tetridentates, or As-As Hexadentates)	Five membered heterocyclic ring(s) containing one arsenic atom. In addition, ligand contains additional arsenic-containing substituents (usually arsines) that constitute As binding sites. Can include other ring systems bound to the heterocyclic ring or to the As-containing substituent, but they do not coordinate with the stabilized, high valence metal ion. Ring(s) can also contain O, N, S, P or Se atoms. This 5-membered ring(s) and/or attached, uncoordinating rings and/or As-containing substituent(s) may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>As Valence Stabilizer #10:</u> Six-Membered Heterocyclic Rings containing One Arsenic Atom and having at least one additional Arsenic Atom Binding Site not in a Ring (As Monodentates, As-As Bidentates, As-As Tridentates, As-As Tetridentates, or As-As Hexadentates)	Six membered heterocyclic ring(s) containing one arsenic atom. In addition, ligand contains additional arsenic-containing substituents (usually arsines) that constitute As binding sites. Can include other ring systems bound to the heterocyclic ring or to the As-containing substituent, but they do not coordinate with the stabilized, high valence metal ion. Ring(s) can also contain O, N, S, P or Se atoms. This 6-membered ring(s) and/or attached, uncoordinating rings and/or As-containing substituent(s) may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>As Valence Stabilizer #11:</u> Five-Membered Heterocyclic Rings containing One Arsenic Atom and having at least one additional Arsenic Atom Binding Site in a separate Ring (As Monodentates, As-As Bidentates, As-As Tridentates, As-	Five membered heterocyclic ring(s) containing one arsenic atom. In addition, ligand contains additional arsenic-containing rings that constitute As binding sites. Can include other ring systems bound to the As-containing heterocyclic rings, but they do not coordinate

As Tetridentates, or As-As Hexadentates)	with the stabilized, high valence metal ion. Ring(s) can also contain O, N, S, P, or Se atoms. This 5-membered ring(s) and/or additional As-containing ring(s) and/or attached, uncoordinating rings may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>As Valence Stabilizer #12:</u> Six-Membered Heterocyclic Rings containing One Arsenic Atom and having at least one additional Arsenic Atom Binding Site in a separate Ring (As Monodentates, As-As Bidentates, As-As Tridentates, As-As Tetridentates, or As-As Hexadentates)	Six membered heterocyclic ring(s) containing one arsenic atom. In addition, ligand contains additional arsenic-containing rings that constitute As binding sites. Can include other ring systems bound to the As-containing heterocyclic rings, but they do not coordinate with the stabilized, high valence metal ion. Ring(s) can also contain O, N, S, P, or Se atoms. This 6-membered ring(s) and/or additional As-containing ring(s) and/or attached, uncoordinating rings may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>As Valence Stabilizer #13:</u> Two-, Three-, Four-, and Six-Membered Macrocyclics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Arsenic and are not contained in Component Heterocyclic Rings (As-As Bidentates, As-As Tridentates, As-As Tetridentates, and As-As Hexadentates)	Macrocyclic ligands containing two, three, four, or six arsenic binding sites to valence stabilize the central metal ion. Can include other hydrocarbon or ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbons/rings may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>As Valence Stabilizer #14:</u> Four-, or Six-Membered Macrocyclics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Arsenic and are contained in Component 5-Membered Heterocyclic Rings (As-As Tridentates, As-As Tetridentates, or As-As Hexadentates)	Macrocyclic ligands containing a total of four or six five-membered heterocyclic rings containing arsenic binding sites. Can include other hydrocarbon/ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbon/rings may or may not have halogen or polarizing or water-insolubilizing groups attached.
<u>As Valence Stabilizer #15:</u> Four-, or Six-Membered Macrocyclics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Arsenic and	Macrocyclic ligands containing at least one 5-membered heterocyclic ring. These heterocyclic rings provide arsenic binding sites to valence stabilize the central metal ion. Other arsine binding sites can also be included in the macrocyclic ligand, so long as the total number

<p>are contained in a Combination of 5-Membered Heterocyclic Rings and Arsine Groups (As-As Tridentates, As-As Tetridentates, or As-As Hexadentates)</p>	<p>of binding sites is four or eight. Can include other hydrocarbon/ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbon/rings may or may not have halogen or polarizing or water-insolubilizing groups attached.</p>
<p><u>As Valence Stabilizer #16:</u> Four-, or Six-Membered Macrocylics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Arsenic and are contained in Component 6-Membered Heterocyclic Rings (As-As Tridentates, As-As Tetridentates, or As-As Hexadentates)</p>	<p>Macrocylic ligands containing a total of four or six six-membered heterocyclic rings containing arsenic binding sites. Can include other hydrocarbon/ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbon/rings may or may not have halogen or polarizing or water-insolubilizing groups attached.</p>
<p><u>As Valence Stabilizer #17:</u> Four-, or Six-Membered Macrocylics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Arsenic and are contained in a Combination of 6-Membered Heterocyclic Rings and Arsine Groups (As-As Tridentates, As-As Tetridentates, or As-As Hexadentates)</p>	<p>Macrocylic ligands containing at least one 6-membered heterocyclic ring. These heterocyclic rings provide arsenic binding sites to valence stabilize the central metal ion. Other arsine binding sites can also be included in the macrocyclic ligand, so long as the total number of binding sites is four or six. Can include other hydrocarbon/ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbon/rings may or may not have halogen or polarizing or water-insolubilizing groups attached.</p>
<p><u>Se Valence Stabilizer #1:</u> Monoselenoethers (Se Monodentates) wherein at least one Selenium Atom is a Binding Site</p>	<p>SeH₂, SeHR, SeR₂, where R represents H or any organic functional group wherein the number of carbon atoms ranges from 0 to 25, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, P, O, S, or Se atoms.</p>
<p><u>Se Valence Stabilizer #2:</u> Diselenoethers (Se-Se Bidentates) wherein at least one Selenium Atom is a Binding Site</p>	<p>R-Se-R'-Se-R'', where R, R', and R'' represents H or any organic functional group wherein the number of carbon atoms ranges from 0 to 25, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, P, O, S, or Se atoms.</p>

<u>Se Valence Stabilizer #3:</u> Triselenoethers (Se-Se Bidentates or Se-Se Tridentates) wherein at least one Selenium Atom is a Binding Site	R-Se-R'-Se-R''-Se-R''', where R, R', R'', and R''' represents H or any organic functional group wherein the number of carbon atoms ranges from 0 to 25, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, P, O, S, or Se atoms.
<u>Se Valence Stabilizer #4:</u> Tetraselenoethers (Se-Se Bidentates, Se-Se Tridentates, or Se-Se Tetridentates) wherein at least one Selenium Atom is a Binding Site	R-Se-R'-Se-R''-Se-R''"-Se-R''''', where R, R', R'', R''', and R'''' represents H or any organic functional group wherein the number of carbon atoms ranges from 0 to 25, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, P, O, S, or Se atoms.
<u>Se Valence Stabilizer #5:</u> Five-Membered Heterocyclic Rings containing One or Two Selenium Atoms wherein at least one Selenium Atom is a Binding Site (Se Monodentates or Se-Se Bidentates)	Five membered heterocyclic ring containing one or two selenium atoms, both of which may function as binding sites. Can include other ring systems bound to this heterocyclic ring, but they do not coordinate with the stabilized, high valence metal ion. Ring can also contain O, N, P, As, or S atoms. This 5-membered ring and/or attached, uncoordinating rings may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>Se Valence Stabilizer #6:</u> Six-Membered Heterocyclic Rings containing One or Two Selenium Atoms wherein at least one Selenium Atom is a Binding Site (Se Monodentates or Se-Se Bidentates)	Six membered heterocyclic ring containing one or two selenium atoms, both of which may function as binding sites. Can include other ring systems bound to this heterocyclic ring, but they do not coordinate with the stabilized, high valence metal ion. Ring can also contain O, N, P, As, or S atoms. This 5-membered ring and/or attached, uncoordinating rings may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>Se Valence Stabilizer #7:</u> Five-Membered Heterocyclic Rings containing One Selenium Atom and having at least one additional Selenium Atom Binding Site not in a Ring (Se Monodentates, Se-Se Bidentates, Se-Se Tridentates, Se-Se Tetridentates, or Se-Se Hexadentates)	Five membered heterocyclic ring(s) containing one selenium atom. In addition, ligand contains additional selenium-containing substituents (usually selenols or selenoethers) that constitute Se binding sites. Can include other ring systems bound to the heterocyclic ring or to the Se-containing substituent, but they do not coordinate with the stabilized, high valence metal ion. Ring(s) can also contain O, N, P, As or S atoms. This 5-membered ring(s) and/or

	attached, uncoordinating rings and/or Se-containing substituent(s) may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>Se Valence Stabilizer #8:</u> Six-Membered Heterocyclic Rings containing One Selenium Atom and having at least one additional Selenium Atom Binding Site not in a Ring (Se Monodentates, Se-Se Bidentates, Se-Se Tridentates, Se-Se Tetridentates, or Se-Se Hexadentates)	Six membered heterocyclic ring(s) containing one selenium atom. In addition, ligand contains additional selenium-containing substituents (usually selenols or selenoethers) that constitute Se binding sites. Can include other ring systems bound to the heterocyclic ring or to the Se-containing substituent, but they do not coordinate with the stabilized, high valence metal ion. Ring(s) can also contain O, N, P, As or S atoms. This 6-membered ring(s) and/or attached, uncoordinating rings and/or Se-containing substituent(s) may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>Se Valence Stabilizer #9:</u> Five-Membered Heterocyclic Rings containing One Selenium Atom and having at least one additional Selenium Atom Binding Site in a separate Ring (Se Monodentates, Se-Se Bidentates, Se-Se Tridentates, Se-Se Tetridentates, or Se-Se Hexadentates)	Five membered heterocyclic ring(s) containing one selenium atom. In addition, ligand contains additional selenium-containing rings that constitute Se binding sites. Can include other ring systems bound to the Se-containing heterocyclic rings, but they do not coordinate with the stabilized, high valence metal ion. Ring(s) can also contain O, N, P, As, or S atoms. This 5-membered ring(s) and/or additional Se-containing ring(s) and/or attached, uncoordinating rings may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>Se Valence Stabilizer #10:</u> Six-Membered Heterocyclic Rings containing One Selenium Atom and having at least one additional Selenium Atom Binding Site in a separate Ring (Se Monodentates, Se-Se Bidentates, Se-Se Tridentates, Se-Se Tetridentates, or Se-Se Hexadentates)	Six membered heterocyclic ring(s) containing one selenium atom. In addition, ligand contains additional selenium-containing rings that constitute Se binding sites. Can include other ring systems bound to the Se-containing heterocyclic rings, but they do not coordinate with the stabilized, high valence metal ion. Ring(s) can also contain O, N, P, As, or S atoms. This 6-membered ring(s) and/or additional Se-containing ring(s) and/or attached, uncoordinating rings may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>Se Valence Stabilizer #11:</u> Two-, Three-, Four-, or Six-Membered	Macrocyclic ligands containing two, three, four, or six selenium binding sites to valence stabilize

<p>Macrocyclics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Selenium (usually selenol or selenoether groups) and are not contained in Component Heterocyclic Rings (Se-Se Bidentates, Se-Se Tridentates, Se-Se Tetridentates, or Se-Se Hexadentates)</p>	<p>the central metal ion. Can include other hydrocarbon or ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbons/rings may or may not have halogen or polarizing or water-insolubilizing/solubilizing groups attached.</p>
<p><u>Se Valence Stabilizer #12:</u> Four-, or Six-Membered Macrocylics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Selenium and are contained in Component 5-Membered Heterocyclic Rings (Se-Se Tridentates, Se-Se Tetridentates or Se-Se Hexadentates)</p>	<p>Macrocylic ligands containing a total of four or six five-membered heterocyclic rings containing selenium binding sites. Can include other hydrocarbon/ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbon/rings may or may not have halogen or polarizing or water-insolubilizing groups attached.</p>
<p><u>Se Valence Stabilizer #13:</u> Four-, or Six-Membered Macrocylics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Selenium and are contained in a Combination of 5-Membered Heterocyclic Rings and Selenol or Selenoether Groups (Se-Se Tridentates, Se-Se Tetridentates, or Se-Se Hexadentates)</p>	<p>Macrocylic ligands containing at least one 5-membered heterocyclic ring. These heterocyclic rings provide selenium binding sites to valence stabilize the central metal ion. Other selenol or selenoether binding sites can also be included in the macrocyclic ligand, so long as the total number of binding sites is four or six. Can include other hydrocarbon/ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbon/rings may or may not have halogen or polarizing or water-insolubilizing groups attached.</p>
<p><u>Se Valence Stabilizer #14:</u> Four-, or Six-Membered Macrocylics, Macrobicyclics, and Macropolycyclics (including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Selenium and are contained in Component 6-Membered Heterocyclic Rings (Se-Se Tridentates, Se-Se Tetridentates, or Se-Se Hexadentates)</p>	<p>Macrocylic ligands containing a total of four or six six-membered heterocyclic rings containing selenium binding sites. Can include other hydrocarbon/ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbon/rings may or may not have halogen or polarizing or water-insolubilizing groups attached.</p>
<p><u>Se Valence Stabilizer #15:</u> Four-, or Six-Membered Macrocylics, Macrobicyclics, and Macropolycyclics</p>	<p>Macrocylic ligands containing at least one 6-membered heterocyclic ring. These heterocyclic rings provide selenium binding</p>

(including Catapinands, Cryptands, Cyclidenes, and Sepulchrates) wherein all Binding Sites are composed of Selenium and are contained in a Combination of 6-Membered Heterocyclic Rings and Selenol or Selenoether Groups (Se-Se Tridentates, Se-Se Tetradentates, or Se-Se Hexadentates)	sites to valence stabilize the central metal ion. Other selenol or selenoether binding sites can also be included in the macrocyclic ligand, so long as the total number of binding sites is four or six. Can include other hydrocarbon/ring systems bound to this macrocyclic ligand, but they do not coordinate with the stabilized, high valence metal ion. This ligand and/or attached, uncoordinating hydrocarbon/rings may or may not have halogen or polarizing or water-insolubilizing groups attached.
<u>Se Valence Stabilizer #16:</u> 1,3-Diselenoketones (Diseleno-beta-ketonates), 1,3,5-Triselenoketones, Bis(1,3-Diselenoketones), and Poly(1,3-Diselenoketones) (S-S Bidentates, S-S Tridentates, S-S Tetradentates)	R-C(=Se)-CR'R"-C(=Se)-R''' where R, R', R'', and R''' represent H, NH ₂ , or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>Se Valence Stabilizer #17:</u> 1,1-Diselenolates, Bis(1,1-diselenolates), and Poly(1,1-diselenolates) (Se-Se Bidentates and Se-Se Tetradentates)	RR'-C=C(-Se)(-Se ⁻), where R and R' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>Se Valence Stabilizer #18:</u> Diselenocarbamates, Bis(diselenocarbamates), and Poly(diselenocarbamates) (including N-hydroxydiselenocarbamates and N-mercaptodiselenocarbamates) (Se-Se Bidentates, Se-Se Tridentates, and Se-Se Tetradentates)	RR'N ⁺ =C(SeH)(SeH), where R and R' represent H, OH, SH, OR'' (R'' = C ₁ -C ₃₀ alkyl or aryl), SR'' (R'' = C ₁ -C ₃₀ alkyl or aryl), NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>Se Valence Stabilizer #19:</u> Triselenophosphoric Acids (Phosphorotriselenoic Acids), Bis(triselenophosphoric acids), Poly(triselenophosphoric acids), and derivatives thereof (Se-Se Bidentates, Se-Se Tridentates, Se-Se Tetradentates)	(O=)P(-Se-R)(-Se-R')(-Se-R'') or (Se=)P(-Se-R)(-Se-R')(-O-R''), where R, R', and R'' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>Se Valence Stabilizer #20:</u> Diselenophosphoric Acids	(O=)P(-Se-R)(-Se-R')(-O-R'') or (Se=)P(-Se-R)(-O-R')(-O-R''), where R, R', and R''

(Phosphorodiselenoic Acids), Bis(diselenophosphoric acids), Poly(diselenophosphoric acids), and derivatives thereof (Se-Se Bidentates, Se-Se Tridentates, Se-Se Tetradentates)	represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>Se Valence Stabilizer #21:</u> Tetraselenophosphoric Acids (Phosphorotetraselenoic Acids), Bis(tetraselenophosphoric acids), Poly(tetraselenophosphoric acids), and derivatives thereof (Se-Se Bidentates, Se-Se Tridentates, Se-Se Tetradentates)	(Se=)P(-Se-R)(-Se-R')(-Se-R''), where R, R', and R'' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>Se Valence Stabilizer #22:</u> Diselenocarbonates, Triselenocarbonates, Bis(diselenocarbonates), and Bis(triselenocarbonates), (Se-Se Bidentates and Se-Se Tetradentates)	R-Se-C(=Se)-O-R' or R-Se-C(=O)-Se-R' for diselenocarbonates, and R-Se-C(=Se)-Se-R' for triselenocarbonates, where R, and R' represent H, NH ₂ or any organic functional group wherein the number of carbon atoms ranges from 0 to 40, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached. Ligand can also contain nonbinding N, O, S, or P atoms.
<u>Se Valence Stabilizer #23:</u> Selenocyanates (Se Monodentates)	Selenocyanates bound directly to the high valence metal ion.
<u>Se Valence Stabilizer #24:</u> Selenolates (Se Monodentates)	Selenolates (HSe-R, HSe-R-SeH, etc.), where R and R' represent H or any organic functional group wherein the number of carbon atoms ranges from 0 to 35, optionally having halogen or polarizing or water-insolubilizing/solubilizing groups attached.
<u>Miscellaneous Valence Stabilizer #1:</u> Diene or bicyclic or tricyclic hydrocarbon ligands	Dialkenes or bicyclic or tricyclic hydrocarbons bound directly to the high valence metal ion.
<u>Miscellaneous Valence Stabilizer #2:</u> Cyanide and related ligands	Cyanide and cyanate and related ligands bound directly to the high valence metal ion.
<u>Miscellaneous Valence Stabilizer #3:</u> Carbonyl ligands	Carbonyl (-CO) ligands bound directly to the high valence metal ion.
<u>Miscellaneous Valence Stabilizer #4:</u> Halogen ligands	Halogen (X) atoms bound directly to the high valence metal ion.
<u>Miscellaneous Valence Stabilizer #5:</u> Hydroxo and Oxo Ligands	Hydroxo and oxo ligands bound directly to the high valence metal ion.

N Valence Stabilizer #1a: Examples of five-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of nitrogen (usually amine or imine groups) and are not contained in component heterocyclic rings (N-N Tridentates or N-N Tetridentates) that meet the requirements
5 for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to:

pentaazacyclodecane ([10]aneN₅); pentaazacycloundecane ([11]aneN₅); pentaazacyclododecane ([12]aneN₅); pentaazacyclotridecane ([13]aneN₅); pentazaacyclotetradecane ([14]aneN₅);
10 pentaazacyclopentadecane ([15]aneN₅); pentaazacyclodecatriene ([10]trieneN₅); pentaazacycloundecatriene ([11]trieneN₅); pentaazacyclododecatriene ([12]trieneN₅);
pentaazacyclotridecatriene ([13]trieneN₅); pentazaacyclotetradecatriene ([14]trieneN₅); and
15 pentaazacyclopentadecatriene ([15]trieneN₅).

N Valence Stabilizer #1b: Examples of seven-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of nitrogen (usually amine or imine groups) and are not contained in component heterocyclic rings (N-N Tridentates, N-N Tetridentates, or N-N Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: heptaazacyclotetradecane ([14]aneN₇); heptaazacyclopentadecane ([15]aneN₇);
heptaazacyclohexadecane ([16]aneN₇); heptaazacycloheptadecane ([17]aneN₇);
20 heptaazacyclooctadecane ([18]aneN₇); heptaazacyclononadecane ([19]aneN₇); heptaazacycloeicosane ([20]aneN₇); heptaazacycloheneicosane ([21]aneN₇);
heptaazacyclotradecatriene ([14]trieneN₇); heptaazacyclopentadecatriene ([15]trieneN₇);
heptaazacyclohexadecatriene ([16]trieneN₇); heptaazacycloheptadecatriene ([17]trieneN₇);
25 heptaazacyclooctadecatriene ([18]trieneN₇); heptaazacyclononadecatriene ([19]trieneN₇); heptaazacycloeicosatriene ([20]trieneN₇); and heptaazacycloheneicosatriene ([21]trieneN₇).

N Valence Stabilizer #1c: Examples of nine-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of nitrogen (usually amine or imine groups) and are not contained in component heterocyclic rings (N-N Tridentates, N-N Tetridentates, or N-N Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not
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limited to: nonaazacyclooctadecane ([18]aneN₉); nonaazacyclononadecane ([19]aneN₉); nonaazacyclocicosane ([20]aneN₉); nonaazacycloheneicosane ([21]aneN₉); nonaazacyclodocosane ([22]aneN₉); nonaazacyclotricosane ([23]aneN₉); nonaazacyclotetracosane ([24]aneN₉); nonaazacyclopentacosane ([25]aneN₉); 5 nonaazacyclohexacosane ([26]aneN₉); nonaazacycloheptacosane ([27]aneN₉); nonaazacyclooctadecatetraene ([18]tetraeneN₉); nonaazacyclononadecatetraene ([19]tetraeneN₉); nonaazacyclocicosatetraene ([20]tetraeneN₉); nonaazacycloheneicosatetraene ([21]tetraeneN₉); nonaazacyclodocosatetraene ([22]tetraeneN₉); nonaazacyclotricosatetraene ([23]tetraeneN₉); 10 nonaazacyclotetracosatetraene ([24]tetraeneN₉); nonaazacyclopentacosatetraene ([25]tetraeneN₉); nonaazacyclohexacosatetraene ([26]tetraeneN₉); and nonaazacycloheptacosatetraene ([27]tetraeneN₉).

15 N Valence Stabilizer #2a: Examples of five-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all five binding sites are composed of nitrogen and are contained in component 5-membered heterocyclic rings (N-N Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: pentaphyrins (pentapyrroles); sapphyrins; smaragdyrins; ptaoxazoles; pentaisooxazoles; pentathiazoles; pentaisothiazoles; 20 pentaazaphospholes; pentaimidazoles; pentapyrazoles; ptaoxadiazoles; pentathiadiazoles; pentadiazaphospholes; pentatriazoles; ptaoxatriazoles; and pentathiatriazoles.

25 N Valence Stabilizer #2b: Examples of seven-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all seven binding sites are composed of nitrogen and are contained in component 5-membered heterocyclic rings (N-N Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: heptaphyrins (heptapyrroles); heptaoxazoles; heptaisooxazoles; heptathiazoles; heptaisothiazoles; heptaazaphospholes; heptaimidazoles; heptapyrazoles; heptaoxadiazoles; heptathiadiazoles; heptadiazaphospholes; 30 heptatriazoles; heptaoxatriazoles; and heptathiatriazoles.

N Valence Stabilizer #3a: Examples of five-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all five binding sites are composed of nitrogen and are contained in a combination of 5-membered heterocyclic rings and amine or imine groups (N-N Tridentates or N-N Tetridentates) that meet
5 the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: superphthalocyanine; supernaphthalocyanine; diazapentaphyrins; tetraazapentaphyrins; pentaazapentaphyrins; diazapentapyrazoles; tetraazapentapyrazoles; pentaazapentapyrazoles; diazapentaimidazoles; tetraazapentaimidazoles; and pentaazapentaimidazoles.

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N Valence Stabilizer #3b: Examples of seven-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all seven binding sites are composed of nitrogen and are contained in a combination of 5-membered heterocyclic rings and amine or imine groups (N-N Tridentates, N-N Tetridentates, or N-N
15 Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diazaheptaphyrins; tetraazaheptaphyrins; hexaazaheptaphyrins; diazaheptapyrazoles; tetraazaheptapyrazoles; hexaazaheptapyrazoles; diazaheptaimidazoles; tetraazaheptaimidazoles; and hexaazaheptaimidazoles.

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N Valence Stabilizer #3c: Examples of nine-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all nine binding sites are composed of nitrogen and are contained in a combination of 5-membered heterocyclic rings and amine or imine groups (N-N Tridentates, N-N Tetridentates, or N-N
25 Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diazanonaphyrins; tetraazanonaphyrins; hexaazanonaphyrins; diazanonapyrazoles; tetraazanonapyrazoles; hexaazanonapyrazoles; diazanonaimidazoles; tetraazanonaimidazoles; and hexaazanonaimidazoles.

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N Valence Stabilizer #4a: Examples of five-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all five binding sites are composed of nitrogen and are contained in component 6-membered

heterocyclic rings (N-N Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: cyclopentapyridines; cyclopentaoxazines; cyclopentathiazines; cyclopentaphosphorins; cyclopentaquinolines; cyclopentapyrazines; cyclopentapyridazines; cyclopentapyrimidines; cyclopentaoxadiazines; 5 cyclopentathiadiazines; cyclopentadiazaphosphorins cyclopentaquinoxalines; cyclopentatriazines; cyclopentathiatriazines; and cyclopentaoxatriazines.

10 N Valence Stabilizer #4b: Examples of seven-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all seven binding sites are composed of nitrogen and are contained in component 6-membered heterocyclic rings (N-N Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: cycloheptapyridines; cycloheptaoxazines; cycloheptathiazines; cycloheptaphosphorins; cycloheptaquinolines; cycloheptapyrazines; cycloheptapyridazines; cycloheptapyrimidines; cycloheptaoxadiazines; 15 cycloheptathiadiazines; cycloheptadiazaphosphorins cycloheptaquinoxalines; cycloheptatriazines; cycloheptathiatriazines; and cycloheptaoxatriazines.

20 N Valence Stabilizer #5a: Examples of five-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all five binding sites are composed of nitrogen and are contained in a combination of 6-membered heterocyclic rings and amine or imine groups (N-N Tridentates or N-N Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diazacyclopentapyridines; tetraazacyclopentapyridines; diazacyclopentaquinolines; tetraazacyclopentaquinolines; diazacyclopentapyrazines; tetraazacyclopentapyrazines; 25 diazacyclopentapyridazines; tetraazacyclopentapyridazines; diazacyclopentapyrimidines; tetraazacyclopentapyrimidines; diazacyclopentatriazines; and tetraazacyclopentatriazines.

30 N Valence Stabilizer #5b: Examples of seven-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all seven binding sites are composed of nitrogen and are contained in a combination of 6-membered heterocyclic rings and amine or imine groups (N-N Tridentates, N-N Tetridentates, or N-N

Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diazacycloheptapyridines; tetraazacycloheptapyridines; diazacycloheptaquinolines; tetraazacycloheptaquinolines; diazacycloheptapyrazines; tetraazacycloheptapyrazines; diazacycloheptapyridazines; tetraazacycloheptapyridazines; 5 diazacycloheptapyrimidines; tetraazacycloheptapyrimidines; diazacycloheptatriazines; and tetraazacycloheptatriazines.

N Valence Stabilizer #5c: Examples of nine-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all 10 nine binding sites are composed of nitrogen and are contained in a combination of 6-membered heterocyclic rings and amine or imine groups (N-N Tridentates, N-N Tetridentates, or N-N Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diazacyclononapyridines; tetraazacyclononapyridines; diazacyclononaquinolines; tetraazacyclononaquinolines; diazacyclononapyrazines; 15 tetraazacyclononapyrazines; diazacyclononapyridazines; tetraazacyclononapyridazines; diazacyclononapyrimidines; tetraazacyclononapyrimidines; diazacyclononatriazines; and tetraazacyclononatriazines.

N Valence Stabilizer #6: Examples of silylamines and silazanes (N Monodentates, N-N Bidentates, N-N Tridentates, N-N Tetridentates, and N-N Hexadentates) that meet the 20 requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: trisilylamine; N-methyldisilazane (disilylmethylamine); N,N-dimethylsilylamine; (silyldimethylamine); tris(trimethylsilyl)amine; triethylsilylamine (triethylaminosilane) (triethylsilazane); N-ethyltriethylsilylamine (triethyl-N-ethylaminosilane); di-tert- 25 butylsilanediamine (di-tert-butylaminosilane); bis(methylamino)diethylsilane; tris(dimethylamino)ethylsilane; hexamethyldisilazane; N-methylhexaphenyldisilazane; hexamethylcyclotrisilazane; and octaphenylcyclotetrasilazane. [Note: silylamines and silazanes are notably weaker ligands than their carbonaceous derivatives, although replacement of one or two SiR₃ groups with CR₃ will enhance the donor power of the ligand. Thus, N(CR₃)₂(SiR₃) is a 30 better ligand than N(CR₃)(SiR₃)₂, etc.]

N Valence Stabilizer #7: Examples of guanidines, diguanidines, and polyguanidines (N-N bidentates, N-N tridentates, N-N tetridentates, and N-N hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: guanidine; methylguanidine; ethylguanidine; isopropylguanidine; butylguanidine; benzylguanidine; phenylguanidine; tolylguanidine; naphthylguanidine; cyclohexylguanidine; norbornylguanidine; adamantlylguanidine; dimethylguanidine; diethylguanidine; diisopropylguanidine; dibutylguanidine; dibenzylguanidine; diphenylguanidine; ditolylguanidine; dinaphthylguanidine; dicyclohexylguanidine; dinorbornylguanidine; diadamantlylguanidine; ethylenediguanidine; propylenediguanidine; tetramethylenediguanidine; pentamethylenediguanidine; hexamethylenediguanidine; heptamethylenediguanidine; octamethylenediguanidine; phenylenediguanidine; piperazinediguanidine; oxalyldiguanidine; malonyldiguanidine; succinyldiguanidine; glutaryldiguanidine; adipyldiguanidine; pimelyldiguanidine; suberyldiguanidine; phthalyldiguanidine; benzimidazoleguanidine; aminoguanidine; nitroaminoguanidine; dicyandiamide (cyanoguanidine); dodecylguanidine; and nitrovin.

N Valence Stabilizer #8: Examples of phosphonitrile amides and bis(phosphonitrile amides) (N-N Bidentates and N-N Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: phosphononitrile amide; N-phenylphosphonitrile amide; N-benzylphosphonitrile amide; N-cyclohexylphosphonitrile amide; N-norbornylphosphonitrile amide; N,N'-diphenylphosphonitrile amide; N,N'-dibenzylphosphonitrile amide; N,N'-dicyclohexylphosphonitrile amide; and N,N'-dinorbornylphosphonitrile amide. [Note: the phosphite (P⁺³) valence of the phosphorus atom makes stabilization of high valence metal ions much more difficult, though still possible.]

N Valence Stabilizer #9: Examples of phosphonimidic diamides, bis(phosphonimidic diamides), and poly(phosphonimidic diamides) (N-N bidentates and N-N tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: phosphonimidic diamide; N-benzylphosphonimidic diamide; N-phenylphosphonimidic diamide; N-cyclohexylphosphonimidic diamide; N-norbornylphosphonimidic diamide; N,N'-dibenzylphosphonimidic diamide; N,N-diphenylphosphonimidic diamide; N,N'-dicyclohexylphosphonimidic diamide; and N,N-dinorbornylphosphonimidic diamide. [Note: the

phosphite (P^{+3}) valence of the phosphorus atom makes stabilization of high valence metal ions much more difficult, though still possible.]

N Valence Stabilizer #10: Examples of phosphonamidimidic acid, phosphonamidimidothioic acid, bis(phosphonamidimidic acid), bis(phosphonamidimidothioic acid), poly(phosphonamidimidic acid), poly(phosphonamidimidothioic acid), and derivatives thereof (N-N Bidentates, and N-N Tetridentates) that meet the requirements for use as "narrow band" valence stabilizers for Ce^{+4} include, but are not limited to: phosphonamidimidic acid, phosphonamidimidothioic acid; O-phenylphosphonamidimidic acid; O-benzylphosphonamidimidic acid; O-cyclohexylphosphonamidimidic acid; O-norbornylphosphonamidimidic acid; S-phenylphosphonamidimidothioic acid; S-benzylphosphonamidimidothioic acid; S-cyclohexylphosphonamidimidothioic acid; and S-norbornylphosphonamidimidothioic acid. [Note: the phosphite (P^{+3}) valence of the phosphorus atom makes stabilization of high valence metal ions much more difficult, though still possible.]

N Valence Stabilizer #11: Examples of pyridinaldimines, bis(pyridinaldimines), and poly(pyridinaldimines) (N-N Bidentates, N-N Tridentates, and N-N Tetridentates) that meet the requirements for use as "narrow band" valence stabilizers for Ce^{+4} include, but are not limited to: pyridylideneaniline [N-(pyridylmethylene)benzenamine]; and (2-pyridyl)benzylideneaniline.

N Valence Stabilizer #12: Examples of hydrazones, bis(hydrazones), and poly(hydrazones) (N Monodentates, N-N Bidentates, N-N Tridentates, and N-N Tetridentates) that meet the requirements for use as "narrow band" valence stabilizers for Ce^{+4} include, but are not limited to: acetaldehyde hydrazone; acetaldehyde phenylhydrazone; acetone hydrazone; acetone phenylhydrazone; pinacolone hydrazone; pinacolone phenylhydrazone; benzaldehyde hydrazone; benzaldehyde phenylhydrazone; naphthaldehyde hydrazone; naphthaldehyde phenylhydrazone; norbornanone hydrazone; norbornanone phenylhydrazone; camphor hydrazone; camphor phenylhydrazone; nopinone hydrazone; nopinone phenylhydrazine; 2-pyridinaldehyde hydrazone; 2-pyridinealdehyde phenylhydrazone; salicylaldehyde hydrazone; salicylaldehyde phenylhydrazone; quinolinaldehyde hydrazone; quinolinaldehyde phenylhydrazone; isatin

dihydrazone; isatin di(phenylhydrazone); camphorquinone dihydrazone; camphorquinone di(phenylhydrazone); and 2-hydrazinobenzimidazole hydrazone.

- 5 N Valence Stabilizer #13: Examples of azo compounds without chelate substitution at the ortho- (for aryl) or alpha- or beta- (for alkyl) positions, bis(azo compounds), or poly(azo compounds) (N Monodentates, N-N Bidentates, or N-N Tridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: azobenzene (diphenyldiazene); p-diaminoazobenzene; p-dimethylaminoazobenzene (butter yellow); methyl orange; Fast Garnet GBC (4'-amino-2,3'-dimethylazobenzene) [Note: non-bonding methyl group in the o-position.]; and Alizarin Yellow R. [Note: azo compounds without chelate substitution at the ortho- (for aryl) or beta- (for alkyl) positions tend to stabilize lower oxidation states in metal ions.]
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- 15 N Valence Stabilizer #14: Examples of formazans, bis(formazans), and poly(formazans) without ortho- hydroxy, carboxy, thiol, mercapto, amino, or hydrazido substitution (N-N Bidentates, N-N Tetridentates, and N-N Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 1,3,5-triphenylformazan; and 1,3,5-naphthylformazan.

- 20 N Valence Stabilizer #15: Examples of hydramides (N-N Bidentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: hydrobenzamide; hydronaphthamide; and hydrosalicylamide.

- 25 N Valence Stabilizer #16: Examples of azines (including ketazines), bis(azines), and poly(azines) without ortho- hydroxy, carboxy, thiol, mercapto, amino, or hydrazido substitution (N-N Bidentates, N-N Tetridentates, and N-N Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: benzalazine; naphthalazine; cyclohexanonazine; and norbornonazine.

- 30 N Valence Stabilizer #17: Examples of Schiff Bases with one Imine (C=N) Group and without ortho- (for aryl constituents) or alpha- or beta- (for alkyl constituents) hydroxy, carboxy,

carbonyl, thiol, mercapto, thiocarbonyl, amino, imino, oximo, diazeno, or hydrazido substitution (N Monodentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: N-(Benzaldehydo)isopropylamine; N-(Naphthaldehydo)isopropylamine; N-(Acetophenono)isopropylamine; N-(Propiophenono)isopropylamine; N-(Benzaldehydo)cyclohexylamine; N-(Naphthaldehydo)cyclohexylamine; N-(Acetophenono)cyclohexylamine; N-(Propiophenono)cyclohexylamine; N-(Benzaldehydo)aniline (BAAN); N-(Naphthaldehydo)aniline; N-(Acetophenono)aniline; N-(Propiophenono)aniline; N-(Benzaldehydo)aminonorbornane; N-(Naphthaldehydo)aminonorbornane; N-(Acetophenono)aminonorbornane; N-(Propiophenono)aminonorbornane; (Vanillino)anisidine; (Cinnamaldehydo)anisidine; N-(o-carboxycinnamaldehydo)aniline; N-(cinnamaldehydo)aniline; N-(cinnamaldehydo)m- or p-anisidine; and N-(o-carboxycinnamaldehydo)m- or p-anisidine.

N Valence Stabilizer #18: Examples of isocyanide and cyanamide and related ligands (N Monodentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: isocyanate (-NCO); isothiocyanate (-NCS); isoselenocyanate (-NCSe); and cyanamide (-NCN). [Note: the nitrogen atom is directly complexed to the high valence metal ion.]

N Valence Stabilizer #19: Examples of nitrosyls and nitrites and related ligands (N Monodentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: nitrosyl (-NO); thionitrosyl (-NS); nitrite (-NO₂); thionitrite (sulfinylamide)(thiazate)(-NSO); nitrosamine (=NN=O); thionitrosamine (=NN=S); nitramine (=NNO₂); and thionitramine (=NNS₂) ligands.

N Valence Stabilizer #20: Examples of nitriles, dinitriles, and polynitriles (N Monodentates, N-N Bidentates, N-N Tridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: benzonitrile; naphthonitrile; cyanonaphthalene; cyclohexyl nitrile; cyanopyridine; cyanopurine; cyanophenol; cyanothiophenol; adamantane nitrile; norbornyl nitrile; cinnamonitrile; dicyanobenzene; dicyanobutene; dicyanoimidazole; dicyanopyridine; cyanotolunitrile; tetracyanoethylene

(TCNE); tetracyanoquinodimethane (TCNQ); diethylaminopropionitrile (deapn), and polyacrylonitriles.

5 N Valence Stabilizer #21: Examples of azide ligands (N monodentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: azide (-N₃) ions; methyl azide; ethyl azide; phenyl azide; diphenyltriazene; and phenyl sulfonyl azide.

10 S Valence Stabilizer #1: Examples of monothioethers (S monodentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: hydrogen sulfide, dimethyl sulfide, diethyl sulfide, dioctyl sulfide, diphenyl sulfide, dicyclohexyl sulfide, tetramethylene sulfide (tetrahydrothiophene, tht), trimethylene sulfide, dimethylene sulfide (ethylene sulfide), pentamethylene sulfide, 1,4-thioxane, oxathiolane, cyclohexene sulfide, cyclooctene sulfide, benzotetrahydrothiophene, dibenzothiophene, 15 naphthotetrahydrothiophene, and thiabicycloheptane.

20 S Valence Stabilizer #2: Examples of disulfides (S monodentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: methyl disulfide, ethyl disulfide, phenyl disulfide, nitrophenide, and 1,2-dithiacyclohexane.

25 S Valence Stabilizer #3: Examples of dithioethers (S monodentates or S-S bidentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 1,3-dithiane, 1,4-dithiane, benzodithiane, dibenzodithiane, naphthodithiane, 2,5-dithiahexane (dth); 3,6-dithiaoctane (dto); 2,5-dimethyl-3,6-dithiaoctane; 3,7-dithianonane; 2,6-dithiaheptane; 1,6-diphenyl-2,5-dithiahexane; 1,4-diphenyl-1,4-dithiabutane; 1,3-dithiolane; 1,4-dithiane (1,4-dithiacyclohexane); 1,4-dithiacycloheptane (dtch); 1,5-dithiacyclooctane (dtco); o-phenylenebis(2-thiapropane); o-phenylenebis(2-thiabutane); 2,2’-(thiamethyl)biphenyl, and 2,2’-(thiaethyl)biphenyl.

30 S Valence Stabilizer #4: Examples of trithioethers (S monodentates, S-S bidentates, or S-S tridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴

include, but are not limited to: 1,3,5-trithiane; 1,3,5-tris(methylthia)cyclohexane; 1,3,5-tris(ethylthia)cyclohexane; 1,3,5-tris(phenylthia)cyclohexane; 2,5,8-trithianonane; 3,6,9-trithiaundecane; and 2,6,10-trithiaundecane.

5 S Valence Stabilizer #5: Examples of tetrathioethers (S monodentates, S-S bidentates, S-S tridentates, or S-S tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 1,4,10,13-tetrathiatridecane; 2,6,10,14-tetrathiapentadecane; 2,5,8,11-tetrathiadodecane; 2,5,9,12-tetrathiatridecane; 2,6,9,13-tetrathiatetradecane; 1,4-(o-thiomethyl)phenyl-1,4-dithiabutane; 1,5-(o-thiomethyl)phenyl-1,5-dithiapentane; 1,6-(o-thiomethyl)phenyl-1,6-dithiahexane; 1,4-(o-thiomethyl)phenyl-1,4-dithiabut-2-ene; and polythioethers.

10 S Valence Stabilizer #6: Examples of hexathioethers (S monodentates, S-S bidentates, S-S tridentates, S-S tetridentates, or S-S hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: tri(2-((o-thiomethyl)phenyl)ethyl)amine; and tri((o-thiomethyl)phenyl)methylamine.

15 S Valence Stabilizer #7a: Examples of 5-membered heterocyclic rings containing one sulfur atom (S monodentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dihydrothiophene, thiophene, thiazole, thiapyrrolidine, thiaphospholene, thiaphosphole, oxathiole, thiadiazole, thiatriazole, benzodihydrothiophene, benzothiophene, benzothiazole, benzothiaphosphole, dibenzothiophene, and naphthothiophene.

20 S Valence Stabilizer #7b: Examples of 5-membered heterocyclic rings containing two sulfur atoms (S monodentates or S-S bidentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dithiole, benzodithiole, and naphthodithiole.

25 S Valence Stabilizer #8a: Examples of 6-membered heterocyclic rings containing one sulfur atom (S monodentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dihydrothiopyran, thiopyran, thiazine, thiadiazine,

thiaphosphorin, thiadiphosphorin, oxathiin, benzothiopyran, dibenzothiopyran, and naphthothiopyran.

S Valence Stabilizer #8b: Examples of 6-membered heterocyclic rings containing two sulfur atoms (S monodentates or S-S bidentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dihydrodithiin, dithiin, benzodithiin, dibenzodithiin (thianthrene), and naphthodithiin.

S Valence Stabilizer #9a: Examples of 5-membered heterocyclic rings containing one sulfur atom and having at least one additional sulfur atom binding site not contained in a ring (S Monodentates, S-S Bidentates, S-S Tridentates, S-S Tetridentates, or S-S Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2,5-dimercapto-2,5-dihydrothiophene; 2,5-bis(thiomethyl)-2,5-dihydrothiophene; 2,5-bis(2-thiophenyl)-2,5-dihydrothiophene; 2,5-dimercaptothiophene; 2,5-bis(thiomethyl)thiophene; 2,5-bis(2-thiophenyl)thiophene; 2,5-dimercatothiazole; 2,5-bis(thiomethyl)thiazole; 2,5-bis(2-thiophenyl)thiazole; 2,5-dimercapto-1,3,4-thiadiazole [bismuththiol]; 2-mercaptophtianaphthene; 7-(thiomethyl)thianaphthene; 1,8-dimercaptodibenzothiophene; 2-mercaptopbenzothiazole; 2-mercapro-1,3,4-thiadiazole; 2-amino-5-mercpto-1,3,4-thiadiazole; 2,5-bis(alkylthio)-1,3,4-thiadiazole; and 7-(thiomethyl)benzothiazole.

S Valence Stabilizer #9b: Examples of 5-membered heterocyclic rings containing two sulfur atoms and having at least one additional sulfur atom binding site not contained in a ring (S Monodentates, S-S Bidentates, S-S Tridentates, S-S Tetridentates, or S-S Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-mercpto-1,3-dithiole; 2-(dimercaptomethyl)-1,3-dithiole; 4,5-dimercapto-1,3-dithiole; 4,5-bis(2-thiophenyl)-1,3-dithiole; 2-mercaptopbenzodithiole; and 7-mercaptopbenzodithiole.

S Valence Stabilizer #10a: Examples of 6-membered heterocyclic rings containing one sulfur atom and having at least one additional sulfur atom binding site not contained in a ring (S Monodentates, S-S Bidentates, S-S Tridentates, S-S Tetridentates, or S-S Hexadentates) that

meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2,6-dimercapto-2,5-dihydrothiopyran; 2,6-bis(thiomethyl)-2,5-dihydrothiopyran; 2,6-bis(2-thiophenyl)-2,5-dihydrothiopyran; 2,6-dimercaptothiopyran; 2,6-bis(thiomethyl)thiopyran; 2,6-bis(2-thiophenyl)thiopyran; 2,6-dimercaptothiazine; 2,6-bis(thiomethyl)thiazine; 2,6-bis(2-thiophenyl)thiazine; 2,6-dimercapto-1,3,5-thiadiazine; 2-mercaptop-1-benzothiopyran; 8-mercaptop-1-benzothiopyran; and 1,9-dimercaptodibenzothiopyran.

S Valence Stabilizer #10b: Examples of 6-membered heterocyclic rings containing two sulfur atoms and having at least one additional sulfur atom binding site not contained in a ring (S

10 Monodentates, S-S Bidentates, S-S Tridentates, S-S Tetridentates, or S-S Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-mercaptop-1,4-dithiin; 2,6-dimercapto-1,4-dithiin; 2,6-bis(2-thiophenyl)-1,4-dithiin; 2,3-dimercapto-1,4-benzodithiin; 5,8-dimercapto-1,4-benzodithiin; 1,8-dimercaptothianthrene; and 1,4,5,8-tetramercaptothianthrene.

15 S Valence Stabilizer #11a: Examples of 5-membered heterocyclic rings containing one sulfur atom and having at least one additional sulfur atom binding site contained in a ring (S

20 Monodentates, S-S Bidentates, S-S Tridentates, S-S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2,2'-bi-2,5-dihydrothiophene; 2,2',2"-tri-2,5-dihydrothiophene; 2,2'-bithiophene; 2,2',2"-trithiophene; 2,2'-bithiazole; 5,5'-bithiazole; 2,2'-bioxathiole; 2,2'-bi-1,3,4-thiadiazole; 2,2'-bithianaphthene; 2,2'-bibenzothiazole; 1,1'-bis(dibenzothiophene); and polythiophenes.

25 S Valence Stabilizer #11b: Examples of 5-membered heterocyclic rings containing two sulfur atoms and having at least one additional sulfur atom binding site contained in a ring (S

Monodentates, S-S Bidentates, S-S Tridentates, S-S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2,2'-bi-1,3-dithiole; 4,4'-bi-1,3-dithiole; 7,7'-bi-1,2-benzodithiole; 3,3'-bi-1,2-benzodithiole; and tetrathiofulvalene.

S Valence Stabilizer #12a: Examples of 6-membered heterocyclic rings containing one sulfur atom and having at least one additional sulfur atom binding site contained in a ring (S Monodentates, S-S Bidentates, S-S Tridentates, S-S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2,2'-bi-2,5-dihydrothiopyran; 2,2',2"-tri-2,5-dihydrothiopyran; 2,2'-bithiopyran; 2,2',2"-trithiopyran; 2,2'-bi-1,4-thiazine; 2,2'-bi-1,3,5-thiadiazine; 2,2'-bi-1-benzothiopyran; and 1,1'-bis(dibenzothiopyran)

S Valence Stabilizer #12b: Examples of 6-membered heterocyclic rings containing two sulfur atoms and having at least one additional sulfur atom binding site contained in a ring (S Monodentates, S-S Bidentates, S-S Tridentates, S-S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2,2'-bi-1,4-dithiin; 2,2'-bi-1,3-dithiin; 5,5'-bi-1,4-benzodithiin; 2,2'-bi-1,3-benzodithiin; and 1,1'-bithianthrene.

S Valence Stabilizer #13a: Examples of two-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein both binding sites are composed of sulfur (usually thiol or thioether groups) and are not contained in component heterocyclic rings (S-S Bidentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dithiacyclobutane ([4]aneS₂); dithiacyclopentane ([5]aneS₂); dithiacyclohexane ([6]aneS₂); dithiacycloheptane ([7]aneS₂); dithiacyclooctane ([8]aneS₂); dithiacyclobutene ([4]eneS₂); dithiacyclopentene ([5]eneS₂); dithiacyclohexene ([6]eneS₂); dithiacycloheptene ([7]eneS₂); dithiacyclooctene ([8]eneS₂); dithiacyclobutadiene ([4]dieneS₂); dithiacyclopentadiene ([5]dieneS₂); dithiacyclohexadiene ([6]dieneS₂); dithiacycloheptadiene ([7]dieneS₂); and dithiacyclooctadiene ([8]dieneS₂).

S Valence Stabilizer #13b: Examples of three-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of sulfur (usually thiol or thioether groups) and are not contained in component heterocyclic rings (S-S Tridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: trithiacyclohexane ([6]aneS₃);

trithiacycloheptane ([7]aneS₃); trithiacyclooctane ([8]aneS₃); trithiacyclononane ([9]aneS₃); trithiacyclodecane ([10]aneS₃); trithiacycloundecane ([11]aneS₃); trithiacyclododecane ([12]aneS₃); trithiacyclohexene ([6]eneS₃); trithiacycloheptene ([7]eneS₃); trithiacyclooctene ([8]eneS₃); trithiacyclononene ([9]eneS₃); trithiacyclodecene ([10]eneS₃); trithiacycloundecene ([11]eneS₃); trithiacyclododecene ([12]eneS₃); trithiacyclohexatriene ([6]trieneS₃); trithiacycloheptatriene ([7]trieneS₃); trithiacyclooctatriene ([8]trieneS₃); trithiacyclononatriene ([9]trieneS₃); trithiacyclodecatriene ([10]trieneS₃); trithiacycloundecatriene ([11]trieneS₃); and trithiacyclododecatriene ([12]trieneS₃).

- 10 S Valence Stabilizer #13c: Examples of four-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of sulfur (usually thiol or thioether groups) and are not contained in component heterocyclic rings (S-S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: tetrathiacyclooctane ([8]aneS₄);
 15 tetrathiacyclononane ([9]aneS₄); tetrathiacyclodecane ([10]aneS₄); tetrathiacycloundecane ([11]aneS₄); tetrathiacyclododecane ([12]aneS₄); tetrathiacyclotridecane ([13]aneS₄); tetrathiacyclotetradecane ([14]aneS₄); tetrathiacyclopentadecane ([15]aneS₄); tetrathiacyclohexadecane ([16]aneS₄); tetrathiacycloheptadecane ([17]aneS₄); tetrathiacyclooctadecane ([18]aneS₄); tetrathiacyclononadecane ([19]aneS₄);
 20 tetrathiacycloeicosane ([20]aneS₄); tetrathiacyclooctadiene ([8]dieneS₄); tetrathiacyclononadiene ([9]dieneS₄); tetrathiacyclodecadiene ([10]dieneS₄); tetrathiacycloundecadiene ([11]dieneS₄); tetrathiacyclododecadiene ([12]dieneS₄); tetrathiacyclotridecadiene ([13]dieneS₄); tetrathiacyclotetradecadiene ([14]dieneS₄); tetrathiacyclopentadecadiene ([15]dieneS₄); tetrathiacyclohexadecadiene ([16]dieneS₄); tetrathiacycloheptadecadiene ([17]dieneS₄);
 25 tetrathiacyclooctadecadiene ([18]dieneS₄); tetrathiacyclononadecadiene ([19]dieneS₄); tetrathiacycloeicosadiene ([20]dieneS₄); tetrathiacyclooctatetraene ([8]tetraeneS₄); tetrathiacyclononetraene ([9]tetraeneS₄); tetrathiacyclodecatetraene ([10]tetraeneS₄); tetrathiacycloundecatetraene ([11]tetraeneS₄); tetrathiacyclododecatetraene ([12]tetraeneS₄); tetrathiacyclotridecatetraene ([13]tetraeneS₄);
 30 tetrathiacyclotetradecatetraene ([14]tetraeneS₄); tetrathiacyclopentadecatetraene ([15]tetraeneS₄); tetrathiacyclohexadecatetraene ([16]tetraeneS₄);

tetrathiacycloheptadecatetraene ([17]tetraS₄); tetrathiacyclooctadecatetraene ([18]tetraS₄); tetrathiacyclononadecatetraene ([19]tetraS₄); and tetrathiacycloicosatetraene ([20]tetraS₄).

- 5 S Valence Stabilizer #13d: Examples of five-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of sulfur (usually thiol or thioether groups) and are not contained in component heterocyclic rings (S-S Tridentates or S-S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to:
- 10 pentathiacyclodecane ([10]aneS₅); pentathiacycloundecane ([11]aneS₅); pentathiacyclododecane ([12]aneS₅); pentathiacyclotridecane ([13]aneS₅); pentathiacyclotradecane ([14]aneS₅); pentathiacyclopentadecane ([15]aneS₅); pentathiacyclodecatriene ([10]trieneS₅); pentathiacycloundecatriene ([11]trieneS₅); pentathiacyclododecatriene ([12]trieneS₅); pentathiacyclotridecatriene ([13]trieneS₅); pentathiacyclotradecatriene ([14]trieneS₅); and
- 15 pentathiacyclopentadecatriene ([15]trieneS₅).

- 20 S Valence Stabilizer #13e: Examples of six-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of sulfur (usually thiol or thioether groups) and are not contained in component heterocyclic rings (S-S Tridentates, S-S Tetridentates, or S-S Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: hexathiacyclododecane ([12]aneS₆); hexathiacyclotridecane ([13]aneS₆); hexathiacyclotradecane ([14]aneS₆); hexathiacyclopentadecane ([15]aneS₆); hexathiacyclohexadecane ([16]aneS₆); hexathiacycloheptadecane ([17]aneS₆); hexathiacyclooctadecane ([18]aneS₆); hexathiacyclononadecane ([19]aneS₆); hexathiacycloicosane ([20]aneS₆); hexathiacycloheneicosane ([21]aneS₆); hexathiacyclodocosane ([22]aneS₆); hexathiacyclotricosane ([23]aneS₆); hexathiacyclotracosane ([24]aneS₆); hexathiacyclododecatriene ([12]trieneS₆); hexathiacyclotridecatriene ([13]trieneS₆); hexathiacyclotradecatriene ([14]trieneS₆);
- 25 hexathiacyclopentadecatriene ([15]trieneS₆); hexathiacyclohexadecatriene ([16]trieneS₆); hexathiacycloheptadecatriene ([17]trieneS₆); hexathiacyclooctadecatriene ([18]trieneS₆);

hexathiacyclononadecatriene ([19]trieneS₆); hexathiacycloicosatriene ([20]trieneS₆); hexathiacyclopheicosatriene ([21]trieneS₆); hexathiacyclodocosatriene ([22]trieneS₆); hexathiacyclotricosatriene ([23]trieneS₆); and hexathiacyclotetracosatriene ([24]trieneS₆).

5 S Valence Stabilizer #13f: Examples of seven-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of sulfur (usually thiol or thioether groups) and are not contained in component heterocyclic rings (S-S Tridentates, S-S Tetridentates, or S-S Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not
10 limited to: heptathiacyclotetradecane ([14]aneS₇); heptathiacyclopentadecane ([15]aneS₇); heptathiacyclohexadecane ([16]aneS₇); heptathiacycloheptadecane ([17]aneS₇); heptathiacyclooctadecane ([18]aneS₇); heptathiacyclononadecane ([19]aneS₇); heptathiacycloicosane ([20]aneS₇); heptathiacycloheneicosane ([21]aneS₇); heptathiacyclotetradecatriene ([14]trieneS₇); heptathiacyclopentadecatriene ([15]trieneS₇);
15 heptathiacyclohexadecatriene ([16]trieneS₇); heptathiacycloheptadecatriene ([17]trieneS₇); heptathiacyclooctadecatriene ([18]trieneS₇); heptathiacyclononadecatriene ([19]trieneS₇); heptathiacycloicosatriene ([20]trieneS₇); and heptathiacycloheneicosatriene ([21]trieneS₇).

20 S Valence Stabilizer #13g: Examples of eight-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of sulfur (usually thiol or thioether groups) and are not contained in component heterocyclic rings (S-S Tridentates, S-S Tetridentates, or S-S Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: octathiacyclohexadecane ([16]aneS₈); octathiacycloheptadecane ([17]aneS₈);
25 octathiacyclooctadecane ([18]aneS₈); octathiacyclononadecane ([19]aneS₈); octathiacycloicosane ([20]aneS₈); octathiacycloheneicosane ([21]aneS₈); octathiacyclodocosane ([22]aneS₈); octathiacyclotricosane ([23]aneS₈); octathiacyclotetracosane ([24]aneS₈); octathiacyclohexadecatetraene ([16]tetraeneS₈); octathiacycloheptadecatetraene ([17]tetraeneS₈); octathiacyclooctadecatetraene ([18]tetraeneS₈);
30 octathiacyclononadecatetraene ([19]tetraeneS₈); octathiacycloicosatetraene ([20]tetraeneS₈); octathiacycloheneicosatetraene ([21]tetraeneS₈);

octathiacyclodocosatetraiene ([22]tetraieneS₈); octathiacyclotricosatetraiene ([23]tetraieneS₈); and octathiacyclotetracosatetraiene ([24]tetraieneS₈).

S Valence Stabilizer #13h: Examples of nine-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of sulfur (usually thiol or thioether groups) and are not contained in component heterocyclic rings (S-S Tridentates, S-S Tetridentates, or S-S Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: nonathiacyclooctadecane ([18]aneS₉); nonathiacyclononadecane ([19]aneS₉); nonathiacycloeicosane ([20]aneS₉); nonathiacycloheneicosane ([21]aneS₉); nonathiacyclodocosane ([22]aneS₉); nonathiacyclotricosane ([23]aneS₉); nonathiacyclotetracosane ([24]aneS₉); nonathiacyclopentacosane ([25]aneS₉); nonathiacyclohexacosane ([26]aneS₉); nonathiacycloheptacosane ([27]aneS₉); nonathiacyclooctadecatetraiene ([18]tetraieneS₉); nonathiacyclononadecatetraiene ([19]tetraieneS₉); nonathiacycloeicosatetraiene ([20]tetraieneS₉); nonathiacycloheneicosatetraiene ([21]tetraieneS₉); nonathiacyclodocosatetraiene ([22]tetraieneS₉); nonathiacyclotricosatetraiene ([23]tetraieneS₉); nonathiacyclotetracosatetraiene ([24]tetraieneS₉); nonathiacyclopentacosatetraiene ([25]tetraieneS₉); nonathiacyclohexacosatetraiene ([26]tetraieneS₉); and nonathiacycloheptacosatetraiene ([27]tetraieneS₉).

S Valence Stabilizer #13i: Examples of ten-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of sulfur (usually thiol or thioether groups) and are not contained in component heterocyclic rings (S-S Tridentates, S-S Tetridentates, or S-S Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: decathiacycloeicosane ([20]aneS₁₀); decathiacycloheneicosane ([21]aneS₁₀); decathiacyclodocosane ([22]aneS₁₀); decathiacyclotricosane ([23]aneS₁₀); decathiacyclotetracosane ([24]aneS₁₀); decathiacyclopentacosane ([25]aneS₁₀); decathiacyclohexacosane ([26]aneS₁₀); decathiacycloheptacosane ([27]aneS₁₀); decathiacyclooctacosane ([28]aneS₁₀); decathiacyclononacosane ([29]aneS₁₀);

decathiacyclotriacontane ([30]aneS₁₀); decathiacycloeicosapentadiene ([20]pentadieneS₁₀); decathiacyclopenteneicosapentadiene ([21]pentadieneS₁₀); decathiacyclodocosapentadiene ([22]pentadieneS₁₀); decathiacyclotricosapentadiene ([23]pentadieneS₁₀); decathiacyclotetracosapentadiene ([24]pentadieneS₁₀); decathiacyclopentacosapentadiene ([25]pentadieneS₁₀); decathiacyclohexacosapentadiene ([26]pentadieneS₁₀); decathiacycloheptacosapentadiene ([27]pentadieneS₁₀); decathiacyclooctacosapentadiene ([28]pentadieneS₁₀); decathiacyclononacosapentadiene ([29]pentadieneS₁₀); and decathiacyclotricontapentadiene ([30]pentadieneS₁₀).

10 S Valence Stabilizer #14a: Examples of four-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all four binding sites are composed of sulfur and are contained in component 5-membered heterocyclic rings (S-S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: tetrathiophenes; tetrathiazoles; 15 tetrathiaphospholes; tetraoxathioles; tetrathiadiazoles; tetrathiatriazoles; and tetradithioles.

20 S Valence Stabilizer #14b: Examples of five-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all five binding sites are composed of sulfur and are contained in component 5-membered heterocyclic rings (S-S Tridentates or S-S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: pentathiophenes; pentathiazoles; pentathiaphospholes; pentaoxathioles; pentathiadiazoles; pentathiatriazoles; and pentadithioles.

25 S Valence Stabilizer #14c: Examples of six-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all six binding sites are composed of sulfur and are contained in component 5-membered heterocyclic rings (S-S Tridentates, S-S Tetridentates, or S-S Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 30 hexathiophenes; hexathiazoles; hexathiaphospholes; hexaoxathioles; hexathiadiazoles; hexathiatriazoles; and hexadithioles.

S Valence Stabilizer #14d: Examples of seven-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all seven binding sites are composed of sulfur and are contained in component 5-membered heterocyclic rings (S-S Tridentates, S-S Tetridentates, or S-S Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: heptathiophenes; heptathiazoles; heptathiaphospholes; heptaoxathioles; heptathiadiazoles; heptathiatriazoles; and heptadithioles.

S Valence Stabilizer #14e: Examples of eight-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all eight binding sites are composed of sulfur and are contained in component 5-membered heterocyclic rings (S-S Tridentates, S-S Tetridentates, or S-S Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: octathiophenes; octathiazoles; octathiaphospholes; octaoxathioles; octathiadiazoles; octathiatriazoles; and octadithioles.

S Valence Stabilizer #14f: Examples of nine-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all nine binding sites are composed of sulfur and are contained in component 5-membered heterocyclic rings (S-S Tridentates, S-S Tetridentates, or S-S Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: nonathiophenes; nonathiazoles; nonathiaphospholes; nonaoxathioles; nonathiadiazoles; nonathiatriazoles; and nonadithioles.

S Valence Stabilizer #14g: Examples of ten-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all ten binding sites are composed of sulfur and are contained in component 5-membered heterocyclic rings (S-S Tridentates, S-S Tetridentates, or S-S Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: decathiophenes; decathiazoles; decathiaphospholes; decaoxathioles; decathiadiazoles; decathiatriazoles; and decadithioles.

S Valence Stabilizer #15a: Examples of four-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all four binding sites are composed of sulfur and are contained in a combination of 5-membered heterocyclic rings and thiol, thioether, or thioketo groups (S-S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dithiatetrathiophenes; tetrathiatetrathiophenes; dithiatetradithioles; and tetrathiatetradithioles.

S Valence Stabilizer #15b: Examples of five-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all five binding sites are composed of sulfur and are contained in a combination of 5-membered heterocyclic rings and thiol, thioether, or thioketo groups (S-S Tridentates or S-S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dithiapentathiophenes; tetrathiapentathiophenes; dithiapentadithioles; and tetrathiapentadithioles.

S Valence Stabilizer #15c: Examples of six-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all six binding sites are composed of sulfur and are contained in a combination of 5-membered heterocyclic rings and thiol, thioether, or thioketo groups (S-S Tridentates, S-S Tetridentates, or S-S Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dithiahexaathiophenes; trithiahexathiophenes; dithiahexadithioles; and trithiahexadithioles.

S Valence Stabilizer #15d: Examples of seven-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all seven binding sites are composed of sulfur and are contained in a combination of 5-membered heterocyclic rings and thiol, thioether, or thioketo groups (S-S Tridentates, S-S Tetridentates, or S-S Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dithiaheptathiophenes; tetrathiaheptathiophenes; dithiaheptadithioles; and tetrathiaheptadithioles.

S Valence Stabilizer #15e: Examples of eight-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all eight binding sites are composed of sulfur and are contained in a combination of 5-membered heterocyclic rings and thiol, thioether, or thioketo groups (S-S Tridentates, S-S Tetridentates, or S-S Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dithiaoctathiophenes; tetrathiaoctathiophenes; dithiaoctadithioles; and tetrathiaoctadithioles.

5 S Valence Stabilizer #15f: Examples of nine-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all nine binding sites are composed of sulfur and are contained in a combination of 5-membered heterocyclic rings and thiol, thioether, or thioketo groups (S-S Tridentates, S-S Tetridentates, or S-S Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: trithianonathiophenes; hexathianonathiophenes; 10 trithianonadithioles; and hexathianonadithioles.

15 S Valence Stabilizer #15g: Examples of ten-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all ten binding sites are composed of sulfur and are contained in a combination of 5-membered heterocyclic rings and thiol, thioether, or thioketo groups (S-S Tridentates, S-S Tetridentates, or S-S Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dithiadecathiophenes; pentathiadecathiophenes; dithiadecadithioles; and pentathiadecadithioles.

20 S Valence Stabilizer #16a: Examples of four-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all four binding sites are composed of sulfur and are contained in component 6-membered heterocyclic rings (S-S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: tetrathiopyrans; tetrathiazines; 25 tetrathiaphosphorins; tetrathiadiphosphorins; tetraoxathiins; and tetradithiins.

S Valence Stabilizer #16b: Examples of five-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all five binding sites are composed of sulfur and are contained in component 6-membered heterocyclic rings (S-S Tridentates or S-S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: pentathiopyrans; pentathiazines; pentathiaphosphorins; pentathiadiphosphorins; ptaoxathiins; and pentadithiins.

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S Valence Stabilizer #16c: Examples of six-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all six binding sites are composed of sulfur and are contained in component 6-membered heterocyclic rings (S-S Tridentates, S-S Tetridentates, or S-S Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: hexathiopyrans; hexathiazines; hexathiaphosphorins; hexathiadiphosphorins; hexaoxathiins; and hexadithiins.

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S Valence Stabilizer #16d: Examples of seven-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all seven binding sites are composed of sulfur and are contained in component 6-membered heterocyclic rings (S-S Tridentates, S-S Tetridentates, or S-S Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: heptathiopyrans; heptathiazines; heptathiaphosphorins; heptathiadiphosphorins; heptaoxathiins; and heptadithiins.

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S Valence Stabilizer #16e: Examples of eight-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all eight binding sites are composed of sulfur and are contained in component 6-membered heterocyclic rings (S-S Tridentates, S-S Tetridentates, or S-S Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: octathiopyrans; octathiazines; octathiaphosphorins; octathiadiphosphorins; octaoxathiins; and octadithiins.

S Valence Stabilizer #16f: Examples of nine-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all nine binding sites are composed of sulfur and are contained in component 6-membered heterocyclic rings (S-S Tridentates, S-S Tetridentates, or S-S Hexadentates) that meet the

5 requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: nonathiopyrans; nonathiazines; nonathiaphosphorins; nonathiadiphosphorins; nonaoxathiins; and nonadithiins.

S Valence Stabilizer #16g: Examples of ten-membered macrocyclics, macrobicyclics, and

10 macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all ten binding sites are composed of sulfur and are contained in component 6-membered heterocyclic rings (S-S Tridentates, S-S Tetridentates, or S-S Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: decathiopyrans; decathiazines; decathiaphosphorins; decathiadiphosphorins; decaoxathiins; and

15 decadithiins.

S Valence Stabilizer #17a: Examples of four-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all four binding sites are composed of sulfur and are contained in a combination of 6-membered

20 heterocyclic rings and thiol, thioether, or thioketo groups (S-S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dithiatetrathiopyrans; tetrathiatetrathiopyrans; dithiatetrathiazines; tetrathiatetrathiazines; dithiatetrathiaphosphorins; tetrathiatetrathiaphosphorins; dithiatetraoxathiins; tetrathiatetraoxathiins; dithiatetradithiins; and tetrathiatetradithiins.

25 S Valence Stabilizer #17b: Examples of five-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all five binding sites are composed of sulfur and are contained in a combination of 6-membered

30 heterocyclic rings and thiol, thioether, or thioketo groups (S-S Tridentates or S-S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dithiapentathiopyrans; tetrathiapentathiopyrans; dithiapentathiazines;

tetrathiapentathiazines; dithiapentathiaphosphorins; tetrathiapentathiaphosphorins; dithiapentaoxathiins; tetrathiapentaoxathiins; dithiapentadithiins; and tetrathiapentadithiins.

S Valence Stabilizer #17c: Examples of six-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all six binding sites are composed of sulfur and are contained in a combination of 6-membered heterocyclic rings and thiol, thioether, or thioketo groups (S-S Tridentates, S-S Tetridentates, or S-S Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dithiahexathiopyrans; trithiahexathiopyrans; dithiahexathiazines; trithiahexathiazines; dithiahexathiaphosphorins; trithiahexathiaphosphorins; dithiahexaoxathiins; trithiahexaoxathiins; dithiahexadithiins; and trithiahexadithiins.

S Valence Stabilizer #17d: Examples of seven-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all seven binding sites are composed of sulfur and are contained in a combination of 6-membered heterocyclic rings and thiol, thioether, or thioketo groups (S-S Tridentates, S-S Tetridentates, or S-S Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dithiaheptathiopyrans; tetrathiaheptathiopyrans; dithiaheptathiazines; tetrathiaheptathiazines; dithiaheptathiaphosphorins; tetrathiaheptathiaphosphorins; dithiaheptaoxathiins; tetrathiaheptaoxathiins; dithiaheptadithiins; and tetrathiaheptadithiins.

S Valence Stabilizer #17e: Examples of eight-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all eight binding sites are composed of sulfur and are contained in a combination of 6-membered heterocyclic rings and thiol, thioether, or thioketo groups (S-S Tridentates, S-S Tetridentates, or S-S Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dithiaoctathiopyrans; tetrathiaoctathiopyrans; dithiaoctathiazines; tetrathiaoctathiazines; dithiaoctathiaphosphorins; tetrathiaoctathiaphosphorins; dithiaoctaoxathiins; tetrathiaoctaoxathiins; dithiaoctaoxathiins; dithiaoctadithiins; and tetrathiaoctadithiins.

S Valence Stabilizer #17f: Examples of nine-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all nine binding sites are composed of sulfur and are contained in a combination of 6-membered heterocyclic rings and thiol, thioether, or thioketo groups (S-S Tridentates, S-S Tetridentates, or S-S Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: trithianonathiopyrans; hexathianonathiopyrans; trithianonathiazines; hexathianonathiazines; trithianonathiaphosphorins; hexathianonathiaphosphorins; trithianonaoxathiins; hexathianonaoxathiins; trithianonadithiins; and hexathianonadithiins.

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S Valence Stabilizer #17g: Examples of ten-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all ten binding sites are composed of sulfur and are contained in a combination of 6-membered heterocyclic rings and thiol, thioether, or thioketo groups (S-S Tridentates, S-S Tetridentates, or S-S Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dithiadecathiopyrans; pentathiadecathiopyrans; dithiadecathiazines; pentathiadecathiazines; dithiadecathiaphosphorins; pentathiadecathiaphosphorins; dithiadecaoxathiins; pentathiadecaoxathiins; dithiadecadithiins; and pentathiadecadithiins.

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S Valence Stabilizer #18: Examples of dithiobiurets (dithioimidodicarbonic diamides), dithioisobiurets, dithiobiureas, trithiotriurets, trithiotriureas, bis(dithiobiurets), bis(dithioisobiurets), bis(dithiobiureas), poly(dithiobiurets), poly(dithioisobiurets), and poly(dithiobiureas) (S-S Bidentates, S-S Tridentates, S-S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dithiobiuret, dithioisobiuret, dithiobiurea, trithiotriuret, trithiotriurea, nitrodithiobiuret, dinitrodithiobiuret, aminodithiobiuret, diaminodithiobiuret, oxydithiobiuret, dioxydithiobiuret, cyanodithiobiuret, methyldithiobiuret, ethyldithiobiuret, isopropyldithiobiuret, phenyldithiobiuret, benzylidithiobiuret, cyclohexyldithiobiuret, norbornyldithiobiuret, adamantlyldithiobiuret, dimethyldithiobiuret, diethylidithiobiuret, diisopropyldithiobiuret,

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diphenyldithiobiuret, dibenzylidithiobiuret, dicyclohexylidithiobiuret, dinorbornyldithiobiuret, and diadamantyldithiobiuret.

S Valence Stabilizer #19: Examples of thioacylthioureas, thioaroylthioureas,
5 bis(thioacylthioureas), bis(thioaroylthioureas), poly(thioacylthioureas), and
poly(thioaroylthioureas) (S-S Bidentates, S-S Tridentates, S-S Tetridentates) that meet the
requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to:
thioformylthiourea, thioacetylthiourea, thiobenzoylthiourea, thiocyclohexoylthiourea,
pentafluorothiobenzoylthiourea, N-methylthioacetylthiourea, N-phenylthiobenzoylthiourea, and
10 N-cyclohexylthiocyclohexoylthiourea.

S Valence Stabilizer #20: Examples of dithioacyl disulfides, bis(dithioacyl disulfides), and
poly(dithioacyl disulfides), (S-S Bidentates, S-S Tridentates, S-S Tetridentates) that meet the
requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to:
15 dithioacetyl disulfide; dithiopropanoyl disulfide; dithiobenzoyl disulfide; and
dithiopentafluorobenzoyl disulfide.

S Valence Stabilizer #21: Examples of tetrathioperoxydicarbonic diamides,
bis(tetrathioperoxydicarbonic diamides), and poly(tetrathioperoxydicarbonic diamides) (S-S
20 Bidentates, S-S Tridentates, S-S Tetridentates) that meet the requirements for use as “narrow
band” valence stabilizers for Ce⁺⁴ include, but are not limited to: tetrathioperoxydicarbonic
diamide; N-phenyltetrathioperoxydicarbonic diamide; N-benzyltetrathioperoxydicarbonic
diamide; N-cyclohexyltetrathioperoxydicarbonic diamide; N-norbornyltetrathioperoxydicarbonic
diamide; N,N'-diphenyltetrathioperoxydicarbonic diamide; N,N'-
25 dibenzyltetrathioperoxydicarbonic diamide; N,N'-dicyclohexyltetrathioperoxydicarbonic
diamide; and N,N'-dinorbornyltetrathioperoxydicarbonic diamide.

S Valence Stabilizer #22: Examples of hexathio-, pentathio-, and tetrathioperoxydicarbonic
acids, bis(hexathio-, pentathio-, and tetrathioperoxydicarbonic acids), poly(hexathio-, pentathio-,
30 and tetrathioperoxydicarbonic acids), and derivatives thereof (S-S Bidentates, S-S Tridentates, S-
S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴

include, but are not limited to: hexathioperoxydicarbonic acid, pentathioperoxydicarbonic acid, tetrathioperoxydicarbonic acid, S-phenylhexathioperoxydicarbonic acid; S-benzylhexathioperoxydicarbonic acid; S-cyclohexylhexathioperoxydicarbonic acid; S-norbornylhexathioperoxydicarbonic acid; S,S'-diphenylhexathioperoxydicarbonic acid; S,S'-dibenzylhexathioperoxydicarbonic acid; S,S'-dicyclohexylhexathioperoxydicarbonic acid; and S,S'-dinorbornylhexathioperoxydicarbonic acid.

S Valence Stabilizer #23: Examples of dithioperoxydiphosphoramides, bis(dithioperoxydiphosphoramides), and poly(dithioperoxydiphosphoramides) (S-S Bidentates, S-S Tridentates, S-S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dithioperoxydiphosphamide, N-methyldithioperoxydiphosphamide, N-isopropylidithioperoxydiphosphamide, N-tert-butylidithioperoxydiphosphamide, N-phenyldithioperoxydiphosphamide, N-pentafluorophenyldithioperoxydiphosphamide, N-benzyldithioperoxydiphosphamide, N-cyclohexyldithioperoxydiphosphamide, N-norbornyldithioperoxydiphosphamide, N,N''-dimethyldithioperoxydiphosphamide, N,N''-diisopropylidithioperoxydiphosphamide, N,N''-di-tert-butylidithioperoxydiphosphamide, N,N''-diphenyldithioperoxydiphosphamide, N,N''-di-pentafluorophenyldithioperoxydiphosphamide, N,N''-dibenzylidithioperoxydiphosphamide, N,N''-dicyclohexyldithioperoxydiphosphamide, and N,N''-dinorbornyldithioperoxydiphosphamide.

S Valence Stabilizer #24: Examples of dithioperoxydiphosphoric acids, bis(dithioperoxydiphosphoric acids), poly(dithioperoxydiphosphoric acids), and derivatives thereof (S-S Bidentates, S-S Tridentates, S-S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dithioperoxydiphosphoric acid, methyldithioperoxydiphosphoric acid, isopropylidithioperoxydiphosphoric acid, tert-butylidithioperoxydiphosphoric acid, phenyldithioperoxydiphosphoric acid, pentafluorophenyldithioperoxydiphosphoric acid, benzylidithioperoxydiphosphoric acid, cyclohexyldithioperoxydiphosphoric acid, norbornyldithioperoxydiphosphoric acid, dimethyldithioperoxydiphosphoric acid, diisopropylidithioperoxydiphosphoric acid, di-tert-butylidithioperoxydiphosphoric acid,

diphenyldithioperoxydiphosphoric acid, di-pentafluorophenyldithioperoxydiphosphoric acid, dibenzylidithioperoxydiphosphoric acid, dicyclohexyldithioperoxydiphosphoric acid, and dinorbornyldithioperoxydiphosphoric acid.

5 S Valence Stabilizer #25: Examples of dithioimidodiphosphonic acids, dithiohydrazidodiphosphonic acids, bis(dithioimidodiphosphonic acids), bis(dithiohydrazidodiphosphonic acids), poly(dithioimidodiphosphonic acids), poly(dithiohydrazidodiphosphonic acids), and derivatives thereof (S-S Bidentates, S-S Tridentates, S-S Tetridentates) that meet the requirements for use as “narrow band” valence
10 stabilizers for Ce⁺⁴ include, but are not limited to: dithioimidodiphosphonic acid, methyldithioimidodiphosphonic acid, isopropyldithioimidodiphosphonic acid, tert-butylidithioimidodiphosphonic acid, phenyldithioimidodiphosphonic acid, pentafluorophenyldithioimidodiphosphonic acid, benzylidithioimidodiphosphonic acid, cyclohexyldithioimidodiphosphonic acid, norbornyldithioimidodiphosphonic acid,
15 dimethyldithioimidodiphosphonic acid, diisopropyldithioimidodiphosphonic acid, di-tert-butylidithioimidodiphosphonic acid, diphenyldithioimidodiphosphonic acid, di-
pentafluorophenyldithioimidodiphosphonic acid, dibenzylidithioimidodiphosphonic acid, dicyclohexyldithioimidodiphosphonic acid, and dinorbornyldithioimidodiphosphonic acid.
[Note: the phosphite (P⁺³) valence of the phosphorus atom makes stabilization of high valence
20 metal ions much more difficult, though still possible.]

5 S Valence Stabilizer #26: Examples of dithioimidodiphosphonamides, dithiohydrazidodiphosphonamides, bis(dithioimidodiphosphonamides), bis(dithiohydrazidodiphosphonamides), poly(dithioimidodiphosphonamides), and poly(dithiohydrazidodiphosphonamides) (S-S Bidentates, S-S Tridentates, S-S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dithioimidodiphosphonamide, N-methyldithioimidodiphosphonamide, N-isopropyldithioimidodiphosphonamide, N-tert-butyldithioimidodiphosphonamide, N-phenyldithioimidodiphosphonamide, N-pentafluorophenyldithioimidodiphosphonamide, N-benzylidithioimidodiphosphonamide, N-cyclohexyldithioimidodiphosphonamide, N-norbornyldithioimidodiphosphonamide, N,N"-dimethyldithioimidodiphosphonamide, N,N"-.

diisopropyldithioimidodiphosphonamide, N,N''-di-tert-butyldithioimidodiphosphonamide, N,N''-diphenyldithioimidodiphosphonamide, N,N''-di-pentafluorophenyldithioimidodiphosphonamide, N,N''-dibenzylidithioimidodiphosphonamide, N,N''-dicyclohexyldithioimidodiphosphonamide, and N,N''-dinorbornyldithioimidodiphosphonamide. [Note: the phosphite (P^{+3}) valence of the phosphorus atom makes stabilization of high valence metal ions much more difficult, though still possible.]

S Valence Stabilizer #27: Examples of dithiodiphosphonamides, bis(dithiodiphosphonamides), and poly(dithiodiphosphonamides) (S-S Bidentates, S-S Tridentates, S-S Tetridentates) that

meet the requirements for use as “narrow band” valence stabilizers for Ce^{+4} include, but are not limited to: dithiodiphosphonamide, N-methyldithiodiphosphonamide, N-

isopropyldithiodiphosphonamide, N-tert-butyldithiodiphosphonamide, N-

phenyldithiodiphosphonamide, N-pentafluorophenyldithiodiphosphonamide, N-

benzylidithiodiphosphonamide, N-cyclohexyldithiodiphosphonamide, N-

norbornyldithiodiphosphonamide, N,N''-dimethyldithiodiphosphonamide, N,N''-

diisopropyldithiodiphosphonamide, N,N''-di-tert-butyldithiodiphosphonamide, N,N''-

diphenyldithiodiphosphonamide, N,N''-di-pentafluorophenyldithiodiphosphonamide, N,N''-

dibenzylidithiodiphosphonamide, N,N''-dicyclohexyldithiodiphosphonamide, and N,N''-

dinorbornyldithiodiphosphonamide. [Note: the phosphite (P^{+3}) valence of the phosphorus atom

makes stabilization of high valence metal ions much more difficult, though still possible.]

S Valence Stabilizer #28: Examples of dithiodiphosphonic acids, bis(dithiodiphosphonic acids),

poly(dithiodiphosphonic acids), and derivatives thereof (S-S Bidentates, S-S Tridentates, S-S

Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce^{+4}

include, but are not limited to: dithiodiphosphonic acid, methyldithiodiphosphonic acid,

isopropyldithiodiphosphonic acid, tert-butyldithiodiphosphonic acid, phenyldithiodiphosphonic

acid, pentafluorophenyldithiodiphosphonic acid, benzylidithiodiphosphonic acid,

cyclohexyldithiodiphosphonic acid, norbornyldithiodiphosphonic acid,

dimethyldithiodiphosphonic acid, diisopropyldithiodiphosphonic acid, di-tert-

butyldithiodiphosphonic acid, diphenyldithiodiphosphonic acid, di-

pentafluorophenyldithiodiphosphonic acid, dibenzylidithiodiphosphonic acid,

dicyclohexyldithiodiphosphonic acid, and dinorbornyldithiodiphosphonic acid. [Note: the phosphite (P^{+3}) valence of the phosphorus atom makes stabilization of high valence metal ions much more difficult, though still possible.]

- 5 S Valence Stabilizer #29: Examples of dithioperoxydiphosphonamides, bis(dithioperoxydiphosphonamides), and poly(dithioperoxydiphosphonamides) (S-S Bidentates, S-S Tridentates, S-S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce^{+4} include, but are not limited to: dithioperoxydiphosphonamide, N-methyldithioperoxydiphosphonamide, N-isopropyldithioperoxydiphosphonamide, N-tert-butylidithioperoxydiphosphonamide, N-phenyldithioperoxydiphosphonamide, N-pentafluorophenyldithioperoxydiphosphonamide, N-benzylidithioperoxydiphosphonamide, N-cyclohexyldithioperoxydiphosphonamide, N-norbornyldithioperoxydiphosphonamide, N,N''-dimethyldithioperoxydiphosphonamide, N,N''-diisopropyldithioperoxydiphosphonamide, N,N''-di-tert-butylidithioperoxydiphosphonamide, N,N''-diphenyldithioperoxydiphosphonamide, N,N''-di-
- 10 pentafluorophenyldithioperoxydiphosphonamide, N,N''-dibenzylidithioperoxydiphosphonamide, N,N''-dicyclohexyldithioperoxydiphosphonamide, and N,N''-dinorbornyldithioperoxydiphosphonamide. [Note: the phosphite (P^{+3}) valence of the phosphorus atom makes stabilization of high valence metal ions much more difficult, though still possible.]
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- 20 S Valence Stabilizer #30: Examples of dithioperoxydiphosphonic acids, bis(dithioperoxydiphosphonic acids), poly(dithioperoxydiphosphonic acids), and derivatives thereof (S-S Bidentates, S-S Tridentates, S-S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce^{+4} include, but are not limited to:
- 25 dithioperoxydiphosphonic acid, methyldithioperoxydiphosphonic acid, isopropyldithioperoxydiphosphonic acid, tert-butylidithioperoxydiphosphonic acid, phenyldithioperoxydiphosphonic acid, pentafluorophenyldithioperoxydiphosphonic acid, benzylidithioperoxydiphosphonic acid, cyclohexyldithioperoxydiphosphonic acid, norbornyldithioperoxydiphosphonic acid, dimethyldithioperoxydiphosphonic acid,
- 30 diisopropyldithioperoxydiphosphonic acid, di-tert-butylidithioperoxydiphosphonic acid, diphenyldithioperoxydiphosphonic acid, di-pentafluorophenyldithioperoxydiphosphonic acid,

dibenzylidithioperoxydiphosphonic acid, dicyclohexylidithioperoxydiphosphonic acid, and dinorbornylidithioperoxydiphosphonic acid. [Note: the phosphite (P^{+3}) valence of the phosphorus atom makes stabilization of high valence metal ions much more difficult, though still possible.]

- 5 S Valence Stabilizer #31: Examples of dithiophosphonic acids (phosphonodithioic acids), bis(dithiophosphonic acids), poly(dithiophosphonic acids), and derivatives thereof (S-S Bidentates, S-S Tridentates, S-S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce^{+4} include, but are not limited to: dithiophosphonic acid, O-phenyldithiophosphonic acid, O-benzylidithiophosphonic acid, O-cyclohexylidithiophosphonic acid, O-norbornylidithiophosphonic acid, O,P-diphenyldithiophosphonic acid, O,P-dibenzylidithiophosphonic acid, O,P-dicyclohexylidithiophosphonic acid, and O,P-dinorbornylidithiophosphonic acid. [Note: the phosphite (P^{+3}) valence of the phosphorus atom makes stabilization of high valence metal ions much more difficult, though still possible.]
- 10 S Valence Stabilizer #32: Examples of trithiophosphonic acids (phosphonotrithioic acids), bis(trithiophosphonic acids), poly(trithiophosphonic acids), and derivatives thereof (S-S Bidentates, S-S Tridentates, S-S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce^{+4} include, but are not limited to: trithiophosphonic acid, S-phenyltrithiophosphonic acid, S-benzyltrithiophosphonic acid, S-cyclohexyltrithiophosphonic acid, S-norbornyltrithiophosphonic acid, S,P-diphenyltrithiophosphonic acid, S,P-dibenzyltrithiophosphonic acid, S,P-dicyclohexyltrithiophosphonic acid, and S,P-dinorbornyltrithiophosphonic acid. [Note: the phosphite (P^{+3}) valence of the phosphorus atom makes stabilization of high valence metal ions much more difficult, though still possible.]
- 15 S Valence Stabilizer #33: Examples of phosphono(dithioperoxo)thioic acids, bis[phosphono(dithioperoxo)thioic acids], poly[phosphono(dithioperoxo)thioic acids], and derivatives thereof (S-S Bidentates, S-S Tridentates, S-S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce^{+4} include, but are not limited to: phosphono(dithioperoxo)thioic acid, O-phenylphosphono(dithioperoxo)thioic acid, O-benzylphosphono(dithioperoxo)thioic acid, O-cyclohexylphosphono(dithioperoxo)thioic acid, O-norbornylphosphono(dithioperoxo)thioic acid, O,P-diphenylphosphono(dithioperoxo)thioic acid,

O,P-dibenzylphosphono(dithioperoxo)thioic acid, O,P-dicyclohexylphosphono(dithioperoxo)thioic acid, and O,P-dinorbornylphosphono(dithioperoxo)thioic acid. [Note: the phosphite (P^{+3}) valence of the phosphorus atom makes stabilization of high valence metal ions much more difficult, though still possible.]

S Valence Stabilizer #34: Examples of phosphono(dithioperoxo)dithioic acids, bis[phosphono(dithioperoxo)dithioic acids], poly[phosphono(dithioperoxo)dithioic acids], and derivatives thereof (S-S Bidentates, S-S Tridentates, S-S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce^{+4} include, but are not limited to: phosphono(dithioperoxo)dithioic acid, S-phenylphosphono(dithioperoxo)dithioic acid, S-benzylphosphono(dithioperoxo)dithioic acid, S-cyclohexylphosphono(dithioperoxo)dithioic acid, S-norbornylphosphono(dithioperoxo)dithioic acid, S,P-diphenylphosphono(dithioperoxo)dithioic acid, S,P-dibenzylphosphono(dithioperoxo)dithioic acid, S,P-dicyclohexylphosphono(dithioperoxo)dithioic acid, and S,P-dinorbornylphosphono(dithioperoxo)dithioic acid. [Note: the phosphite (P^{+3}) valence of the phosphorus atom makes stabilization of high valence metal ions much more difficult, though still possible.]

S Valence Stabilizer #35: Examples of S-(alkylthio)thiocarboxylic acids, S-(arylthio)thiocarboxylic acids, and S,S-thiobisthiocarboxylic Acids (S-S Bidentates and S-S Tridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce^{+4} include, but are not limited to: (methylthio)thioacetic acid; (methylthio)thiobenzoic acid; (methylthio)thionicotinic acid; (methylthio)thionaphthoic acid; (phenylthio)thioacetic acid; (phenylthio)thiobenzoic acid; (phenylthio)thionaphthoic acid; (norbornylthio)thioacetic acid; (norbornylthio)thiobenzoic acid; (norbornylthio)thionaphthoic acid; thiobisthioacetic acid; thiobisthiobenzoic acid; and thiobisthionaphthoic acid.

S Valence Stabilizer #36: Examples of S-(alkyldisulfido)thiocarboxylic acids, S-(aryldisulfido)thiocarboxylic acids, and S,S'-disulfidobisthiocarboxylic acids (S-S Bidentates and S-S Tridentates) that meet the requirements for use as “narrow band” valence stabilizers for

Ce⁺⁴ include, but are not limited to: (methyldisulfido)thioacetic acid; (methyldisulfido)thiobenzoic acid; (methyldisulfido)thionicotinic acid; (methyldisulfido)thionaphthoic acid; (phenyldisulfido)thioacetic acid; (phenyldisulfido)thiobenzoic acid; (phenyldisulfido)thionaphthoic acid; (norbornyldisulfido)thioacetic acid; (norbornyldisulfido)thiobenzoic acid; (norbornyldisulfido)thionaphthoic acid; S,S'-disulfidobisthioacetic acid; S,S'-disulfidobisthiobenzoic acid; and S,S'-disulfidobisthionaphthoic acid.

S Valence Stabilizer #37: Examples of 1,2-dithiolates, bis(1,2-dithiolates), and poly(1,2-dithiolates) (S-S Bidentates, S-S Tridentates, S-S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2,3-butanedithiol; 1,2-diphenyl-1,2-ethanedithiol; 1,2-di(pentafluorophenyl)-1,2-ethanedithio; 1,2-dicyclohexyl-1,2-ethanedithiol; 1,2-dinorbornyl-1,2-ethanedithiol; 2,3-dimercaptopropanol; 2,3-dimercaptosuccinic acid; poly[bis(arylthio)acetylene]s; and poly[bis(alkylylthio)acetylene]s.

S Valence Stabilizer #38: Examples of rhodanines and bis(rhodanines) (S-S Bidentates and S-S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 3-methylrhodanine; 3-ethylrhodanine; 3-isopropylrhodanine; 3-phenylrhodanine; 3-benzylrhodanine; 3-cyclohexylrhodanine; 3-norbornylrhodanine; 5-methylrhodanine; 5-ethylrhodanine; 5-isopropylrhodanine; 5-phenylrhodanine; 5-benzylrhodanine; 5-cyclohexylrhodanine; 5-norbornylrhodanine; 3,3'-ethylenebisrhodanine; 3,3'-propylenerhodanine; 3,3'-butylenenerhodanine; 5,5'-ethylenebisrhodanine; 5,5'-propylenerhodanine; and 5,5'-butylenenerhodanine. [Note: rhodanines and bis(rhodanines) tend to stabilize lower oxidation states in metal ions.]

S Valence Stabilizer #39: Examples of dithiocarbimates, bis(dithiocarbimates), and poly(dithiocarbimates) (S-S Bidentates, S-S Tridentates, and S-S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: methyldithiocarbimate; trifluoromethyldithiocarbimate; ethyldithiocarbimate; propyldithiocarbimate; isopropyldithiocarbimate; butyldithiocarbimate; tertbutyldithiocarbimate; cyanodithiocarbimate (CDC); cyanamidodithiocarbimate; azidodithiocarbimate;

phenyldithiocarbimate; pentafluorophenyldithiocarbimate; benzylidithiocarbimate; naphthyldithiocarbimate; cyclohexyldithiocarbimate; norbornyldithiocarbimate; and adamantlyldithiocarbimate. [Note: carbimates tend to stabilize lower oxidation states in metal ions.]

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S Valence Stabilizer #40: Examples of thioxanthates, bis(thioxanthates), and poly(thioxanthates) (S-S Bidentates and S-S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: methyl thioxanthate (MeSxan); ethyl thioxanthate (EtSxan); isopropyl thioxanthate (iPrSxan); trifluoromethyl thioxanthate (CF₃Sxan); cyanothioxanthate; cyanamidothioxanthate; phenyl thioxanthate (PhSxan); benzyl thioxanthate (BzSxan); pentafluorophenyl thioxanthate; cyclohexyl thioxanthate (cHxSxan); and norbornyl thioxanthate. [Note: thioxanthates tend to stabilize lower oxidation states in metal ions.]

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S Valence Stabilizer #41: Examples of xanthates, bis(xanthates), and poly(xanthates) (S-S Bidentates and S-S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: methyl xanthate (Mexan); ethyl xanthate (Etxan); isopropyl xanthate (iPrxan); trifluoromethyl xanthate (CF₃xan); cyanoxanthate; cyanamidoxanthate; phenyl xanthate (Phxan); benzyl xanthate (Bzxan); pentafluorophenyl xanthate; cyclohexyl xanthate (cHxxan); and norbornyl xanthate. [Note: xanthates tend to stabilize lower oxidation states in metal ions.]

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S Valence Stabilizer #42: Examples of phosphinodithioformates (S-S Bidentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: trimethylphosphinodithioformate; triethylphosphinodithioformate; triphenylphosphinodithioformate; tricyclohexylphosphinodithioformate; dimethylphosphinodithioformate; diethylphosphinodithioformate; diphenylphosphinodithioformate; and dicyclohexylphosphinodithioformate.

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S Valence Stabilizer #43: Examples of alkyl- and aryl- dithioborates, trithioborates, perthioborates, bis(dithioborates), bis(trithioborates), and bis(perthioborates) (S-S Bidentates and S-S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for

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Ce⁺⁴ include, but are not limited to: S,O-diethyl dithioborate; S,O-diisopropyl dithioborate; S,O-diphenyl dithioborate; S,O-dibenzyl dithioborate; S,O-dicyclohexyl dithioborate; S,O-dinorbornyl dithioborate; diethyl trithioborate; diisopropyl trithioborate; diphenyl trithioborate; dibenzyl trithioborate; dicyclohexyl trithioborate; and dinorbornyl trithioborate.

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S Valence Stabilizer #44: Examples of alkyl- and aryl- dithioboronates and bis(dithioboronates) (S-S Bidentates and S-S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diethyl dithioboronate; diisopropyl dithioboronate; diphenyl dithioboronate; dibenzyl dithioboronate; dicyclohexyl dithioboronate; and dinorbornyl dithioboronate. [Note: boronates tend to stabilize lower oxidation states in metal ions.]

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S Valence Stabilizer #45: Examples of trithioarsonic acids (arsonotrithioic acids), dithioarsonic acids (arsonodithioic acids), tetrathioarsonic acids (arsonotetrathioic acids), and derivatives thereof (S-S Bidentates, S-S Tridentates, S-S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: trithioarsonic acid, O-phenyltrithioarsonic acid, O-benzyltrithioarsonic acid, O-cyclohexyltrithioarsonic acid, O-norbornyltrithioarsonic acid, O,S-diphenyltrithioarsonic acid, O,S-dibenzyltrithioarsonic acid, O,S-dicyclohexyltrithioarsonic acid, O,S-dinorbornyltrithioarsonic acid; dithioarsonic acid, O-phenyldithioarsonic acid, O-benzyldithioarsonic acid, O-cyclohexyldithioarsonic acid, O-norbornyldithioarsonic acid, O,O-diphenyldithioarsonic acid, O,O-dibenzylidithioarsonic acid, O,O-dicyclohexyldithioarsonic acid, and O,O-dinorbornyldithioarsonic acid.

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S Valence Stabilizer #46: Examples of trithioantimonic acids (stibonotrithioic acids), dithioantimonic acids (stibonodithioic acids), tetrathioantimonic acids (stibonotetrathioic acids), and derivatives thereof (S-S Bidentates, S-S Tridentates, S-S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: trimethyltrithioantimonate; triethyltrithioantimonate; and triphenyltrithioantimonate.

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S Valence Stabilizer #47: Examples of phosphine P-sulfides and amino-substituted phosphine sulfides (S Monodentates) that meet the requirements for use as “narrow band” valence

stabilizers for Ce⁺⁴ include, but are not limited to: trimethylphosphine sulfide (TMPS); triethylphosphine sulfide (TEPS); triphenylphosphine sulfide (TPhPS); tribenzylphosphine sulfide (TBzPS); tricyclohexylphosphine sulfide (TcHxPS); and trinorbornylphosphine sulfide for phosphine P-sulfides; and tris(dimethylamino)phosphine sulfide; trimorpholinophosphine sulfide; tripiperidinophosphine sulfide; tripyrrolidinophosphine sulfide; and tri(cyclohexylamino)phosphine sulfide for amino-substituted phosphine sulfides.

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S Valence Stabilizer #48: Examples of arsine As-sulfides and amino-substituted arsine sulfides (S Monodentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: trimethylarsine sulfide; triethylarsine sulfide; triphenylarsine sulfide; tribenzylarsine sulfide; tricyclohexylarsine sulfide; and trinorbornylarsine sulfide for arsine As-sulfides; and tris(dimethylamino)arsine sulfide; trimorpholinoarsine sulfide; tripiperidinoarsine sulfide; tripyrrolidinoarsine sulfide; and tri(cyclohexylamino)arsine sulfide for amino-substituted arsine sulfides.

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S Valence Stabilizer #49: Examples of thiolates that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: thiophenol; naphthalenethiol; 1-dodecanethion; hexadecyl mercaptan; benzenethiol (bt); polybenzenethiols; and polythioarylenes.

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S Valence Stabilizer #50: Examples of sulfide that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: sulfides (-S²⁻); disulfides (-S₂²⁻); and polysulfides (-S_x²⁻).

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P Valence Stabilizer #1: Examples of monophosphines (P monodentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: phosphine, phenylphosphine, diphenylphosphine, triphenylphosphine, tricyclohexylphosphine, phenyldimethylphosphine, phenyldiethylphosphine, methylidiphenylphosphine, ethyldiphenylphosphine, phosphirane, phosphetane, phospholane, phosphorinane, benzophospholane, benzophosphorinane, dibenzophospholane, dibenzophosphorinane, naphthophospholane, naphthophosphorinane, phosphinonorbornane, and phosphinoadamantane.

P Valence Stabilizer #2: Examples of diphosphines (P monodentates or P-P bidentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diphospholane, benzodiphospholane, naphthodiphospholane, diphosphorinane, benzodiphosphorinane, dibenzodiphosphorinane, naphthodiphosphorinane, bis(diphenylphosphino)methane, bis(diphenylphosphino)ethane, bis(diphenylphosphino)propane, bis(diphenylphosphino)butane, bis(diphenylphosphino)pentane, 1,2-bis(diphenylphosphino)ethylene, and o-phenylenebis(diphenylphosphine). [Note: the aryl derivatives are air-stable, whereas the alkyl derivatives are air-sensitive and therefore unsuitable for these applications.]

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P Valence Stabilizer #3: Examples of triphosphines (P monodentates, P-P bidentates, or P-P tridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: triphosphorinane, P,P'-tetraphenyl-2-methyl-2-(P-diphenyl)phosphinomethyl-1,3-propanediphosphine; P,P-[2-(P-diphenyl)phosphinoethyl]diethyl-P-phenylphosphine; P,P-[2-(P-diphenyl)phosphino]diphenyl-P-phenylphosphine; and hexahydro-2,4,6-trimethyl-1,3,5-triphosphazine. [Note: the aryl derivatives are air-stable, whereas the alkyl derivatives are air-sensitive and therefore unsuitable for these applications.]

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P Valence Stabilizer #4: Examples of tetraphosphines (P monodentates, P-P bidentates, P-P tridentates, and P-P tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: P,P'-tetraphenyl-2,2-[(P-diphenyl)phosphinomethyl]-1,3-propanediphosphine; tri[o-(P-diphenyl)phosphinophenyl]phosphine; and 1,1,4,7,10,10-hexaphenyl-1,4,7,10-tetraphosphadecane. [Note: the aryl derivatives are air-stable, whereas the alkyl derivatives are air-sensitive and therefore unsuitable for these applications.]

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P Valence Stabilizer #5: Examples of pentaphosphines (P monodentates, P-P bidentates, P-P tridentates, and P-P tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 4-[2-(P-diphenyl)phosphinoethyl]-1,1,7,10,10-pentaphenyl-1,4,7,10-tetraphosphadecane. [Note: the aryl derivatives are air-stable, whereas the alkyl derivatives are air-sensitive and therefore unsuitable for these applications.]

P Valence Stabilizer #6: Examples of hexaphosphines (P-P bidentates, P-P tridentates, P-P tetridentates, and P-P hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 1,1,10,10-tetraphenyl-4,7-[2-(P,P-diphenyl)phosphinoethyl]-1,4,7,10-tetraphosphadecane. [Note: the aryl derivatives are air-stable, whereas the alkyl derivatives are air-sensitive and therefore unsuitable for these applications.]

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P Valence Stabilizer #7a: Examples of 5-membered heterocyclic rings containing one phosphorus atom (P monodentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 1-phospholene, 2-phospholene, 3-phospholene, phosphole, oxaphosphole, thiaphosphole, benzophospholene, benzophosphole, benzoxaphosphole, benzothiaphosphole, dibenzophospholene, dibenzophosphole, naphthophospholene, naphthophosphole, naphthoxaphosphole, naphthothiaphosphole.

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P Valence Stabilizer #7b: Examples of 5-membered heterocyclic rings containing two phosphorus atoms (P monodentates or P-P bidentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diphospholene, diphosphole, oxadiphospholene, thiadiphospholene, benzodiphospholene, benzodiphosphole, naphthodiphospholene, and naphthodiphosphole.

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P Valence Stabilizer #7c: Examples of 5-membered heterocyclic rings containing three phosphorus atoms (P monodentates or P-P bidentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: triphosphole.

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P Valence Stabilizer #8a: Examples of 6-membered heterocyclic rings containing one phosphorus atom (P monodentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: phosphorin, oxaphosphorin, thiaphosphorin, benzophosphorin, benzoxaphosphorin, benzothiaphosphorin, acridophosphine, phosphanthridine, dibenzoxaphosphorin, dibenzothiaphosphorin, naphthophosphorin, naphthoxaphosphorin, and naphthothiaphosphorin.

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P Valence Stabilizer #8b: Examples of 6-membered heterocyclic rings containing two phosphorus atoms (P monodentates or P-P bidentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: o-diphosphorin, m-diphosphorin, p-diphosphorin, oxadiphosphorin, thiadiphosphorin, benzodiphosphorin, 5 benzoxadiphosphorin, benzothiadiphosphorin, dibenzodiphosphorin, dibenzoxadiphosphorin, dibenzothiadiphosphorin, naphthodiphosphorin, naphthoxadiphosphorin, and naphthothiadiphosphorin.

10 P Valence Stabilizer #8c: Examples of 6-membered heterocyclic rings containing three phosphorus atoms (P monodentates or P-P bidentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 1,3,5-triphosphorin, 1,2,3-triphosphorin, benzo-1,2,3-triphosphorin, and naphtho-1,2,3-triphosphorin.

15 P Valence Stabilizer #9a: Examples of 5-membered heterocyclic rings containing one phosphorus atom and having at least one additional phosphorus atom binding site not contained in a ring (P Monodentates, P-P Bidentates, P-P Tridentates, P-P Tetridentates, or P-P Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-(P-phenylphosphino)-1-phospholene; 2,5-(P-phenylphosphino)-1-phospholene; 2-(P-phenylphosphino)-3-phospholene; 2,5-(P-phenylphosphino)-3-phospholene; 20 2-(P-phenylphosphino)phosphole; 2,5-(P-phenylphosphino)phosphole; 2-(P-phenylphosphino)benzophosphole; 7-(P-phenylphosphino)benzophosphole; and 1,8-(P-phenylphosphino)dibenzophosphole.

25 P Valence Stabilizer #9b: Examples of 5-membered heterocyclic rings containing two phosphorus atoms and having at least one additional phosphorus atom binding site not contained in a ring (P Monodentates, P-P Bidentates, P-P Tridentates, P-P Tetridentates, or P-P Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-(P-phenylphosphino)-1,3-diphospholene; 2,5-(P-phenylphosphino)-1,3-diphospholene; 2-(P-phenylphosphino)-1,3-diphosphole; 2,5-(P-phenylphosphino)-1,3-diphosphole; 2-(P-phenylphosphino)benzodiphosphole; and 7-(P-phenylphosphino)benzodiphosphole.

P Valence Stabilizer #9c: Examples of 5-membered heterocyclic rings containing three phosphorus atoms and having at least one additional phosphorus atom binding site not contained in a ring (P Monodentates, P-P Bidentates, P-P Tridentates, P-P Tetridentates, or P-P Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-(P-phenylphosphino)-1,3,4-triphosphole; and 2,5-(P-phenylphosphino)-1,3,4-triphosphole.

P Valence Stabilizer #10a: Examples of 6-membered heterocyclic rings containing one phosphorus atom and having at least one additional phosphorus atom binding site not contained in a ring (P Monodentates, P-P Bidentates, P-P Tridentates, P-P Tetridentates, or P-P Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-(P-phenylphosphino)phosphorin; 2,5-(P-phenylphosphino)phosphorin; 2-(P-phenylphosphino)benzophosphorin; 7-(P-phenylphosphino)benzophosphorin; and 1,9-(P-phenylphosphino)acridophosphine.

P Valence Stabilizer #10b: Examples of 6-membered heterocyclic rings containing two phosphorus atoms and having at least one additional phosphorus atom binding site not contained in a ring (P Monodentates, P-P Bidentates, P-P Tridentates, P-P Tetridentates, or P-P Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-(P-phenylphosphino)-4-diphosphorin; 2,6-(P-phenylphosphino)-4-diphosphorin; 2,3,5,6-(P-phenylphosphino)-4-diphosphorin; 2-(P-phenylphosphino)benzo-1,4-diphosphorin; 2,3-(P-phenylphosphino)benzo-1,4-diphosphorin; 2,8-(P-phenylphosphino)benzo-1,4-diphosphorin; 2,3,5,8-(P-phenylphosphino)benzo-1,4-diphosphorin; 1,9-(P-phenylphosphino)dibenzodiphosphorin; and 1,4,6,9-(P-phenylphosphino)dibenzodiphosphorin.

P Valence Stabilizer #10c: Examples of 6-membered heterocyclic rings containing three phosphorus atoms and having at least one additional phosphorus atom binding site not contained in a ring (P Monodentates, P-P Bidentates, P-P Tridentates, P-P Tetridentates, or P-P Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-(P-phenylphosphino)-1,3,5-triphosphorin; 2,6-(P-

phenylphosphino)-1,3,5-triphosphorin; 4-(P-phenylphosphino)-1,2,3-triphosphorin; and 8-(P-phenylphosphino)benzo-1,2,3-triphosphorin.

P Valence Stabilizer #11a: Examples of 5-membered heterocyclic rings containing one phosphorus atom and having at least one additional phosphorus atom binding site contained in a ring (P Monodentates, P-P Bidentates, P-P Tridentates, P-P Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2,2'-bi-1-phospholene; 2,2',2"-tri-1-phospholene; 2,2'-bi-3-phospholene; 2,2', 2"-tri-3-phospholene; 2,2'-biphosphole; 2,2',2"-triphosphole; and 2,2'-bibenzophosphole.

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P Valence Stabilizer #11b: Examples of 5-membered heterocyclic rings containing two phosphorus atoms and having at least one additional phosphorus atom binding site contained in a ring (P Monodentates, P-P Bidentates, P-P Tridentates, P-P Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2,2'-bi-1,3-diphospholene; 2,2'-bi-1,3-diphosphole; and 2,2'-bibenzo-1,3-diphosphole.

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P Valence Stabilizer #11c: Examples of 5-membered heterocyclic rings containing three phosphorus atoms and having at least one additional phosphorus atom binding site contained in a ring (P Monodentates, P-P Bidentates, P-P Tridentates, P-P Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2,2'-bi-1,3,4-triphosphole; and 2,2',2"-tri-1,3,4-triphosphole.

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P Valence Stabilizer #12a: Examples of 6-membered heterocyclic rings containing one phosphorus atom and having at least one additional phosphorus atom binding site contained in a ring (P Monodentates, P-P Bidentates, P-P Tridentates, P-P Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2,2'-biphosphorin; 2,2',2"-triphosphorin; 2,2',2",2""-tetraphosphorin; 2,2'-bibenzophosphorin; and 8,8'-bibenzophosphorin.

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P Valence Stabilizer #12b: Examples of 6-membered heterocyclic rings containing two phosphorus atoms and having at least one additional phosphorus atom binding site contained in a

ring (P Monodentates, P-P Bidentates, P-P Tridentates, P-P Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 3,3'-bi-1,2-diphosphorin; 3,3',3"-tri-1,2-diphosphorin; 2,2'-bi-1,4-diphosphorin; 2,2',2"-tri-1,4-diphosphorin; 3,3'-bibenzo-1,2-diphosphorin; 8,8'-bibenzo-1,2-diphosphorin; 2,2'-bibenzo-1,4-diphosphorin; and 8,8'-bibenzo-1,4-diphosphorin.

5 P Valence Stabilizer #12c: Examples of 6-membered heterocyclic rings containing three phosphorus atoms and having at least one additional phosphorus atom binding site contained in a ring (P Monodentates, P-P Bidentates, P-P Tridentates, P-P Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 10 2,2'-bi-1,3,5-triphosphorin; 2,2',2"-tri-1,3,5-triphosphorin; 4,4'-bi-1,2,3-triphosphorin; 4,4'-bibenzo-1,2,3-triphosphorin; and 8,8'-bibenzo-1,2,3-triphosphorin.

15 P Valence Stabilizer #13a: Examples of two-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein both binding sites are composed of phosphorus and are not contained in component heterocyclic rings (P-P Bidentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: P,P-diphenyldiphosphacyclobutane ([4]aneP₂); P,P-diphenyldiphosphacyclopentane ([5]aneP₂); P,P-diphenyldiphosphacyclohexane ([6]aneP₂); P,P-diphenyldiphosphacycloheptane ([7]aneP₂); P,P-diphenyldiphosphacyclooctane ([8]aneP₂); P,P-diphenyldiphosphacyclobutene ([4]eneP₂); P,P-diphenyldiphosphacyclopentene ([5]eneP₂); P,P-diphenyldiphosphacyclohexene ([6]eneP₂); P,P-diphenyldiphosphacycloheptene ([7]eneP₂); and P,P-diphenyldiphosphacyclooctene ([8]eneP₂). 20

25 P Valence Stabilizer #13b: Examples of three-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of phosphorus and are not contained in component heterocyclic rings (P-P Tridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: P,P,P-triphenyltriphosphacyclohexane ([6]aneP₃); P,P,P-triphenyltriphosphacycloheptane ([7]aneP₃); P,P,P-triphenyltriphosphacyclooctane ([8]aneP₃); P,P,P-triphenyltriphosphacyclononane ([9]aneP₃); P,P,P-triphenyltriphosphacyclodecane 30

([10]aneP₃); P,P,P-triphenyltriphenyltriphosphacycloundecane ([11]aneP₃); P,P,P-triphenyltriphenyltriphosphacyclododecane ([12]aneP₃); P,P,P-triphenyltriphenyltriphosphacyclohexatriene ([6]trieneP₃); P,P,P-triphenyltriphenyltriphosphacycloheptatriene ([7]trieneP₃); P,P,P-triphenyltriphenyltriphosphacyclooctatriene ([8]trieneP₃); P,P,P-triphenyltriphenyltriphosphacyclononatriene ([9]trieneP₃); P,P,P-triphenyltriphenyltriphosphacyclodecatriene ([10]trieneP₃); P,P,P-triphenyltriphenyltriphosphacycloundecatriene ([11]trieneP₃); and P,P,P-triphenyltriphenyltriphosphacyclododecatriene ([12]trieneP₃).

P Valence Stabilizer #13c: Examples of four-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of phosphorus and are not contained in component heterocyclic rings (P-P Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: P,P,P,P-tetraphenyltetraphosphacyclooctane ([8]aneP₄); P,P,P,P-tetraphenyltetraphosphacyclononane ([9]aneP₄); P,P,P,P-tetraphenyltetraphosphacyclodecane ([10]aneP₄); P,P,P,P-tetraphenyltetraphosphacycloundecane ([11]aneP₄); P,P,P,P-tetraphenyltetraphosphacyclododecane ([12]aneP₄); P,P,P,P-tetraphenyltetraphosphacyclotridecane ([13]aneP₄); P,P,P,P-tetraphenyltetraphosphacyclotetradecane ([14]aneP₄); P,P,P,P-tetraphenyltetraphosphacyclopentadecane ([15]aneP₄); P,P,P,P-tetraphenyltetraphosphacyclohexadecane ([16]aneP₄); P,P,P,P-tetraphenyltetraphosphacycloheptadecane ([17]aneP₄); P,P,P,P-tetraphenyltetraphosphacyclooctadecane ([18]aneP₄); P,P,P,P-tetraphenyltetraphosphacyclononadecane ([19]aneP₄); and P,P,P,P-tetraphenyltetraphosphacycloeicosane ([20]aneP₄).

P Valence Stabilizer #13d: Examples of five-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of phosphorus and are not contained in component heterocyclic rings (P-P Tridentates, or P-P Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: P,P,P,P,P-pentaphenylpentaphosphacyclodecane ([10]aneP₅); P,P,P,P,P-

pentaphenylpentaphosphacycloundecane ([11]aneP₅); P,P,P,P,P-
pentaphenylpentaphosphacyclododecane ([12]aneP₅); P,P,P,P,P-
pentaphenylpentaphosphacyclotridecane ([13]aneP₅); P,P,P,P,P-
pentaphenylpentaphosphacyclotetradecane ([14]aneP₅); and P,P,P,P,P-
5 pentaphenylpentaphosphacyclopentadecane ([15]aneP₅).

P Valence Stabilizer #13e: Examples of six-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of phosphorus and are not contained in component heterocyclic rings (P-P-P Tridentates, P-P-P-P Tetradentates, or P-P-P-P-P-P Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to:
10 P,P,P,P,P-hexaphenylhexaphosphacyclododecane ([12]aneP₆); P,P,P,P,P,P-
hexaphenylhexaphosphacyclotridecane ([13]aneP₆); P,P,P,P,P,P-
hexaphenylhexaphosphacyclotetradecane ([14]aneP₆); P,P,P,P,P,P-
15 hexaphenylhexaphosphacyclopentadecane ([15]aneP₆); P,P,P,P,P,P-
hexaphenylhexaphosphacyclohexadecane ([16]aneP₆); P,P,P,P,P,P-
hexaphenylhexaphosphacycloheptadecane ([17]aneP₆); P,P,P,P,P,P-
hexaphenylhexaphosphacyclooctadecane ([18]aneP₆); P,P,P,P,P,P-
hexaphenylhexaphosphacyclononadecane ([19]aneP₆); P,P,P,P,P,P-
20 hexaphenylhexaphosphacycloicosane ([20]aneP₆); P,P,P,P,P,P-
hexaphenylhexaphosphacycloheneicosane ([21]aneP₆); P,P,P,P,P,P-
hexaphenylhexaphosphacyclodocosane ([22]aneP₆); P,P,P,P,P,P-
hexaphenylhexaphosphacyclotricosane ([23]aneP₆); P,P,P,P,P,P-
hexaphenylhexaphosphacyclotetracosane ([24]aneP₆).
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P Valence Stabilizer #13f: Examples of eight-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of phosphorus and are not contained in component heterocyclic rings (P-P Tridentates, P-P Tetradentates, or P-P Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: P,P,P,P,P,P,P,P-
30 octaphenylloctaphosphacyclohexadecane ([16]aneP₈); P,P,P,P,P,P,P,P-

octaphenyl octaphosphacycloheptadecane ([17]aneP₈); P,P,P,P,P,P,P-P-
octaphenyl octaphosphacyclooctadecane ([18]aneP₈); P,P,P,P,P,P,P-P-
octaphenyl octaphosphacyclononadecane ([19]aneP₈); P,P,P,P,P,P,P-P-
octaphenyl octaphosphacycloicosane ([20]aneP₈); P,P,P,P,P,P,P,P-P-
5 octaphenyl octaphosphacycloheneicosane ([21]aneP₈); P,P,P,P,P,P,P,P-P-
octaphenyl octaphosphacyclodocosane ([22]aneP₈); P,P,P,P,P,P,P,P-P-
octaphenyl octaphosphacyclotricosane ([23]aneP₈); and P,P,P,P,P,P,P,P-P-
octaphenyl octaphosphacyclotetracosane ([24]aneP₈).

10 P Valence Stabilizer #14a: Examples of four-membered macrocyclics, macrobicyclics, and
macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all
four binding sites are composed of phosphorus and are contained in component 5-membered
heterocyclic rings (P-P Tetridentates) that meet the requirements for use as “narrow band”
valence stabilizers for Ce⁺⁴ include, but are not limited to: tetraphospholenes; tetraphospholes;
15 tetraoxaphospholes; tetradiphospholenes; tetradiphospholes; and tetraoxadiphospholes.

20 P Valence Stabilizer #14b: Examples of six-membered macrocyclics, macrobicyclics, and
macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all
six binding sites are composed of phosphorus and are contained in component 5-membered
heterocyclic rings (P-P Tetridentates and P-P Hexadentates) that meet the requirements for use
as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: hexaphospholenes;
hexaphospholes; hexaoxaphospholes; hexadiphospholenes; hexadiphospholes; and
hexaoxadiphospholes.

25 P Valence Stabilizer #14c: Examples of eight-membered macrocyclics, macrobicyclics, and
macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all
eight binding sites are composed of phosphorus and are contained in component 5-membered
heterocyclic rings (P-P Tridentates; P-P Tetridentates; or P-P Hexadentates) that meet the
requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to:
30 octaphospholenes; octaphospholes; octaoxaphospholes; octadiphospholenes; octadiphospholes;
and octaoxadiphospholes.

P Valence Stabilizer #15a: Examples of four-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all four binding sites are composed of phosphorus and are contained in a combination of 5-membered heterocyclic rings and phosphine groups (P-P Tridentates, P-P Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diphosphatetraphospholenes; tetraphosphatetraphospholenes; diphosphatetraphospholes; tetraphosphatetraphospholes; diphoshatetradiphospholes; and tetraphospatetradiphospholes.

10 P Valence Stabilizer #15b: Examples of six-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all six binding sites are composed of phosphorus and are contained in a combination of 5-membered heterocyclic rings and phosphine groups (P-P Tridentates, P-P Tetridentates, and P-P Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diphosphahexaphospholenes; triaphosphahexaphospholenes; diphosphahexaphospholes; triphosphahexaphospholes; diphoshahexadiphospholes; and triphosphahexadiphospholes.

20 P Valence Stabilizer #15c: Examples of eight-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all eight binding sites are composed of phosphorus and are contained in a combination of 5-membered heterocyclic rings and phosphine groups (P-P Tridentates, P-P Tetridentates, and P-P Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diphosphaoctaphospholenes; tetraphosphaoctaphospholenes; diphosphaoctaphospholes; tetraphosphaoctaphospholes; diphoshaoctadiphospholes; and tetraphosphaoctadiphospholes.

30 P Valence Stabilizer #16a: Examples of four-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all four binding sites are composed of phosphorus and are contained in component 6-membered heterocyclic rings (P-P Tetridentates) that meet the requirements for use as “narrow band”

valence stabilizers for Ce⁺⁴ include, but are not limited to: cyclotetraphosphorins; cyclotetraaoxaphosphorins; cyclotetradiphosphorins; and cyclotetraoxadiphosphorins.

5 P Valence Stabilizer #16b: Examples of six-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all six binding sites are composed of phosphorus and are contained in component 6-membered heterocyclic rings (P-P Tridentates, P-P Tetridentates, and P-P Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: cyclohexaphosphorins; cyclohexaoxaphosphorins; cyclohexadiphosphorins; and

10 cyclohexaoxadiphosphorins.

15 P Valence Stabilizer #16c: Examples of eight-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all eight binding sites are composed of phosphorus and are contained in component 6-membered heterocyclic rings (P-P Tridentates, P-P Tetridentates, and P-P Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: cyclooctaphosphorins; cyclooctaoxaphosphorins; cyclooctadiphosphorins; and cyclooctaoxadiphosphorins.

20 P Valence Stabilizer #17a: Examples of four-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all four binding sites are composed of phosphorus and are contained in a combination of 6-membered heterocyclic rings and phosphine groups (P-P Tridentates, P-P Tetridentates, or P-P Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diphosphacyclotetraphosphorins; tetraphosphacyclotetraphosphorins; diphosphacyclotetraoxaphosphorins; tetraphosphacyclotetraoxaphosphorins; diphosphacyclotetradiphosphorins; tetraphosphacyclotetradiphosphorins; diphosphacyclotetraoxadiphosphorins; and tetraphosphacyclotetraoxadiphosphorins.

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P Valence Stabilizer #17b: Examples of six-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all six binding sites are composed of phosphorus and are contained in a combination of 6-membered heterocyclic rings and phosphine groups (P-P Tridentates, P-P Tetridentates, or P-P Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diphosphacyclohexaphosphorins; triphosphacyclohexaphosphorins; diphosphacyclohexaoxaphosphorins; triphosphacyclohexaoxaphosphorins; diphosphacyclohexadiphosphorins; triphosphacyclohexadiphosphorins; diphosphacyclohexaoxadiphosphorins; and triphosphacyclohexaoxadiphosphorins.

P Valence Stabilizer #17c: Examples of eight-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all eight binding sites are composed of phosphorus and are contained in a combination of 6-membered heterocyclic rings and phosphine groups (P-P Tridentates, P-P Tetridentates, or P-P Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diphosphacyclooctaphosphorins; tetraphosphacyclooctaphosphorins; diphosphacyclooctaoxaphosphorins; tetraphosphacyclooctaoxaphosphorins; diphosphacyclooctadiphosphorins; tetraphosphacyclooctadiphosphorins; diphosphacyclooctaoxadiphosphorins; and tetraphosphacyclooctaoxadiphosphorins.

O Valence Stabilizer #1: Examples of dithioperoxydicarbonic acids, bis(dithioperoxydicarbonic acids), poly(dithioperoxydicarbonic acids), and derivatives thereof (O-O Bidentates, O-O Tridentates, O-O Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dithioperoxydicarbonic acid, O-phenyldithioperoxydicarbonic acid; O-benzyldithioperoxydicarbonic acid; O-cyclohexyldithioperoxydicarbonic acid; O-norbornyldithioperoxydicarbonic acid; O,O'-diphenyldithioperoxydicarbonic acid; O,O'-dibenzyldithioperoxydicarbonic acid; O,O'-dicyclohexyldithioperoxydicarbonic acid; and O,O'-dinorbornyldithioperoxydicarbonic acid.

O Valence Stabilizer #2: Examples of imidodiphosphonic acids, hydrazidodiphosphonic acids, bis(imidodiphosphonic acids), bis(hydrazidodiphosphonic acids), poly(imidodiphosphonic acids), poly(hydrazidodiphosphonic acids), and derivatives thereof (O-O Bidentates, O-O Tridentates, O-O Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: imidodiphosphonic acid, methylimidodiphosphonic acid, isopropylimidodiphosphonic acid, tert-butylimidodiphosphonic acid, phenylimidodiphosphonic acid, pentafluorophenylimidodiphosphonic acid, benzylimidodiphosphonic acid, cyclohexylimidodiphosphonic acid, norbornylimidodiphosphonic acid, dimethylimidodiphosphonic acid, diisopropylimidodiphosphonic acid, di-tert-butylimidodiphosphonic acid, diphenylimidodiphosphonic acid, di-pentafluorophenylimidodiphosphonic acid, dibenzylimidodiphosphonic acid, dicyclohexylimidodiphosphonic acid, and dinorbornylimidodiphosphonic acid. [Note: the phosphite (P⁺³) valence of the phosphorus atom makes stabilization of high valence metal ions much more difficult, though still possible.]

O Valence Stabilizer #3: Examples of imidodiphophonamides, hydrazidodiphophonamides, bis(imidodiphophonamides), bis(hydrazidodiphophonamides), poly(imidodiphophonamides), and poly(hydrazidodiphophonamides) (O-O Bidentates, O-O Tridentates, O-O Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: imidodiphophonamide, N-methylimidodiphophonamide, N-isopropylimidodiphophonamide, N-tert-butylimidodiphophonamide, N-phenylimidodiphophonamide, N-pentafluorophenylimidodiphophonamide, N-benzylimidodiphophonamide, N-cyclohexylimidodiphophonamide, N-norbornylimidodiphophonamide, N,N"-dimethylimidodiphophonamide, N,N"-diisopropylimidodiphophonamide, N,N"-di-tert-butylimidodiphophonamide, N,N"-diphenylimidodiphophonamide, N,N"-di-pentafluorophenylimidodiphophonamide, N,N"-dibenzylimidodiphophonamide, N,N"-dicyclohexylimidodiphophonamide, and N,N"-dinorbornylimidodiphophonamide. [Note: the phosphite (P⁺³) valence of the phosphorus atom makes stabilization of high valence metal ions much more difficult, though still possible.]

O Valence Stabilizer #4: Examples of diphosphonamides, bis(diphosphonamides), and poly(diphosphonamides) (O-O Bidentates, O-O Tridentates, O-O Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diphosphonamide, N-methyldiphosphonamide, N-isopropyldiphosphonamide, N-tert-
5 butyldiphosphonamide, N-phenyldiphosphonamide, N-pentafluorophenyldiphosphonamide, N-benzyldiphosphonamide, N-cyclohexyldiphosphonamide, N-norbornyldiphosphonamide, N,N''-dimethyldiphosphonamide, N,N''-diisopropyldiphosphonamide, N,N''-di-tert-butylidiphosphonamide, N,N''-diphenyldiphosphonamide, N,N''-di-
10 pentafluorophenyldiphosphonamide, N,N''-dibenzylidiphosphonamide, N,N''-dicyclohexyldiphosphonamide, and N,N''-dinorbornyldiphosphonamide. [Note: the phosphite (P⁺³) valence of the phosphorus atom makes stabilization of high valence metal ions much more difficult, though still possible.]

O Valence Stabilizer #5: Examples of carbazates (carbazides), bis(carbazates), and poly(carbazates) (O-O Bidentates, O-O Tridentates, and O-O Tetridentates; or possibly N-O Bidentates, N-O Tridentates, and N-O Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: N,N'-dimethylcarbazate; N,N'-di(trifluoromethyl)carbazate; N,N'-diethylcarbazate; N,N'-diphenylcarbazate; N,N'-dibenzylcarbazate; N,N'-di(pentafluorophenyl)carbazate; N,N'-dicyclohexylcarbazate; and N,N'-dinorbornylcarbazate.
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O Valence Stabilizer #6: Examples of arsonic acids, bis(arsonic acids), poly(arsonic acids), and derivatives thereof (O-O Bidentates, O-O Tridentates, O-O Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to:
25 arsonic acid, O-phenylarsonic acid, O-benzylarsonic acid, O-cyclohexylarsonic acid, O-norbornylarsonic acid, O,O-diphenylarsonic acid, O,O-dibenzylarsonic acid, O,O-dicyclohexylarsonic acid, O,O-dinorbornylarsonic acid; and aminophenylarsonic acids.

O Valence Stabilizer #7: Examples of alkyl- and aryl- borates and bis(borates) (O-O Bidentates and O-O Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers
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for Ce⁺⁴ include, but are not limited to: triethyl borate; diisopropyl borate; diphenyl borate; dibenzyl borate; dicyclohexyl borate; and dinorbornyl borate.

O Valence Stabilizer #8: Examples of alkyl- and aryl- boronates and bis(boronates) (O-O Bidentates and O-O Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diethyl boronate; diisopropyl boronate; diphenyl boronate; dibenzyl boronate; dicyclohexyl boronate; and dinorbornyl boronate. [Note: boronates tend to stabilize lower oxidation states in metal ions.]

O Valence Stabilizer #9: Examples of phosphine P-oxides and amino-substituted phosphine oxides (O Monodentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: trimethylphosphine oxide (TMPO); triethylphosphine oxide (TEPO); triphenylphosphine oxide (TPhPO); tribenzylphosphine oxide (TBzPO); tricyclohexylphosphine oxide (TcHxPO); and trinorbornylphosphine oxide for phosphine P-oxides; and hexamethylphosphoramide (HMPA); trimorpholinophosphine oxide (TMrPO); tripiperidinophosphine oxide; tripyrrolidinophosphine oxide; and tri(cyclohexylamino)phosphine oxide for amino-substituted phosphine oxides.

O Valence Stabilizer #10: Examples of arsine As-oxides and amino-substituted arsine oxides (O Monodentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: trimethylarsine oxide (TMA₃O); triethylarsine oxide (TEAsO); triphenylarsine oxide (TPhAsO); tribenzylarsine oxide (TBzAsO); tricyclohexylarsine oxide (TcHxAsO); and trinorbornylarsine oxide for arsine As-oxides; and hexamethylarsonamide; trimorpholinoarsine oxide; tripiperidinoarsine oxide; tripyrrolidinoarsine oxide; and tri(cyclohexylamino)arsine oxide for amino-substituted arsine oxides.

O Valence Stabilizer #11a: Examples of 5-membered heterocyclic rings containing one oxygen atom (O monodentate) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: furan, dihydrofuran, oxazole, isoxazole, oxadiazole, oxatriazole, oxathiole, benzofuran, benzodihydrofuran, benzoxazole, benzisoxazole, benzoxadiazole (benzofurazan), dibenzofuran, dibenzoxazole, dibenzisoxazole, naphthofuran,

naphthoxazole, naphthisoxazole, and naphthoxadiazole.

O Valence Stabilizer #11b: Examples of 5-membered heterocyclic rings containing two oxygen atoms (O monodentate or O-O bidentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dioxolane, benzodioxolane, and naphthodioxolane.

O Valence Stabilizer #12a: Examples of 6-membered heterocyclic rings containing one oxygen atom (O monodentate) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dihydropyran, pyran, oxazine, oxadiazine, oxatriazine, oxathiin, benzopyran, benzoxazine, benzoxadiazine, dibenzopyran, naphthopyran, naphthoxazine, and naphthoxadiazine.

O Valence Stabilizer #12b: Examples of 6-membered heterocyclic rings containing two oxygen atoms (O monodentate or O-O bidentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dihydriodioxane, dioxane, benzodioxane, dibenzodioxane, and naphthodioxane.

O Valence Stabilizer #13a: Examples of 5-membered heterocyclic rings containing one oxygen atom and having at least one additional oxygen atom binding site not contained in a ring (O monodentates, O-O bidentates, O-O tridentates, O-O tetridentates, or O-O hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2,5-dihydroxy-2,5-dihydrofuran; 2,5-bis(hydroxymethyl)-2,5-dihydrofuran; 2,5-bis(2-hydroxyphenyl)-2,5-dihydrofuran; 2,5-dihydroxyfuran; 2,5-bis(hydroxymethyl)furan; and 2,5-bis(2-hydroxyphenyl)furan.

O Valence Stabilizer #13b: Examples of 5-membered heterocyclic rings containing two oxygen atoms and having at least one additional oxygen atom binding site not contained in a ring (O monodentates, O-O bidentates, O-O tridentates, O-O tetridentates, or O-O hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-hydroxy-1,3-dioxolane; 2-hydroxymethyl)-1,3-dioxolane; 4,5-dihydroxy-1,3-

dioxolane; 4,5-bis(2-hydroxyphenyl)-1,3-dioxolane; 2-hydroxybenzodioxolane; and 7-hydroxybenzodioxolane.

O Valence Stabilizer #14a: Examples of 6-membered heterocyclic rings containing one oxygen atom and having at least one additional oxygen atom binding site not contained in a ring (O monodentates, O-O bidentates, O-O tridentates, O-O tetridentates, or O-O hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2,6-dihydroxy-2,5-dihydropyran; 2,6-bis(hydroxymethyl)-2,5-dihydropyran; 2,6-bis(2-hydroxyphenyl)-2,5-dihydropyran; 2,6-dihydroxypyran; 2,6-bis(hydroxymethyl)pyran; 2,6-bis(2-hydroxyphenyl)pyran; 2-hydroxy-1-benzopyran; 8-hydroxy-1-benzopyran; and 1,9-dihydroxydibenzopyran.

O Valence Stabilizer #14b: Examples of 6-membered heterocyclic rings containing two oxygen atoms and having at least one additional oxygen atom binding site not contained in a ring (O monodentates, O-O bidentates, O-O tridentates, O-O tetridentates, or O-O hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-hydroxy-1,4-dioxane; 2,6-dihydroxy-1,4-dioxane; 2,6-bis(2-hydroxyphenyl)-1,4-dioxane; 2,3-dihydroxy-1,4-benzodioxane; 5,8-dihydroxy-1,4-benzodioxane; 1,8-dihydroxydibenzodioxane; and 1,4,5,8-tetrahydroxydibenzodioxane.

O Valence Stabilizer #15a: Examples of 5-membered heterocyclic rings containing one oxygen atom and having at least one additional oxygen atom binding site contained in a ring (O monodentates, O-O bidentates, O-O tridentates, O-O tetridentates, or O-O hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2,2'-bi-2,5-dihydrofuran; 2,2',2"-tri-2,5-dihydrofuran; 2,2'-bifuran; 2,2',2"-trifuran; 1,1'-bis(dibenzofuran); and polyfurans.

O Valence Stabilizer #15b: Examples of 5-membered heterocyclic rings containing two oxygen atoms and having at least one additional oxygen atom binding site contained in a ring (O monodentates, O-O bidentates, O-O tridentates, O-O tetridentates, or O-O hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not

limited to: 2,2'-bi-1,3-dioxolane; 4,4'-bi-1,3-dioxolane; 7,7'-bi-1,2-benzodioxolane; and 3,3'-bi-1,2-benzodioxolane.

O Valence Stabilizer #16a: Examples of 6-membered heterocyclic rings containing one oxygen atom and having at least one additional oxygen atom binding site contained in a ring (O monodentates, O-O bidentates, O-O tridentates, O-O tetridentates, or O-O hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2,2'-bi-2,5-dihydropyran; 2,2',2"-tri-2,5-dihydropyran; 2,2'-bipyran; 2,2',2"—tripyran; and 1,1'-bis(dibenzopyran).

O Valence Stabilizer #16b: Examples of 6-membered heterocyclic rings containing one oxygen atom and having at least one additional oxygen atom binding site contained in a ring (O monodentates, O-O bidentates, O-O tridentates, O-O tetridentates, or O-O hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2,2'-bi-1,4-dioxane; 2,2'-bi-1,3-dioxane; 5,5'-bi-1,4-benzodioxane; and 2,2'-bi-1,3-benzodioxane.

O Valence Stabilizer #17a: Examples of four-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of oxygen (usually ester or hydroxyl groups) and are not contained in component heterocyclic rings (O-O Bidentates, O-O Tridentates, O-O Tetridentates, and O-O Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 8-crown-4; 10-crown-4; 12-crown-4; 14-crown-4; 16-crown-4; 18-crown-4; 20-crown-4; dibenzo-8-crown-4; dibenzo-10-crown-4; dibenzo-12-crown-4; dibenzo-14-crown-4; dibenzo-16-crown-4; dibenzo-18-crown-4; dibenzo-20-crown-4; tetrabenzo-8-crown-4; tetrabenzo-10-crown-4; tetrabenzo-12-crown-4; tetrabenzo-14-crown-4; tetrabenzo-16-crown-4; tetrabenzo-18-crown-4; and tetrabenzo-20-crown-4.

O Valence Stabilizer #17b: Examples of five-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of oxygen (usually ester or hydroxyl groups) and are not contained in

component heterocyclic rings (O-O Bidentates, O-O Tridentates, O-O Tetridentates, and O-O Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 10-crown-5; 15-crown-5; 20-crown-5; 25-crown-5; pentabenzo-10-crown-5; pentabenzo-15-crown-5; pentabenzo-20-crown-5; and pentabenzo-25-crown-5.

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O Valence Stabilizer #17c: Examples of six-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of oxygen (usually ester or hydroxyl groups) and are not contained in component heterocyclic rings (O-O Bidentates, O-O Tridentates, O-O Tetridentates, and O-O Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 12-crown-6; 18-crown-6; 24-crown-6; 30-crown-6; 36-crown-6; tribenzo-12-crown-6; tribenzo-18-crown-6; tribenzo-24-crown-6; tribenzo-30-crown-6; tribenzo-36-crown-6; hexabenzo-12-crown-6; hexabenzo-18-crown-6; hexabenzo-24-crown-6; hexabenzo-30-crown-6; and hexabenzo-36-crown-6.

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O Valence Stabilizer #17d: Examples of seven-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of oxygen (usually ester or hydroxyl groups) and are not contained in component heterocyclic rings (O-O Bidentates, O-O Tridentates, O-O Tetridentates, and O-O Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 14-crown-7; 21-crown-7; 28-crown-7; 35-crown-7; heptabenzo-14-crown-7; heptabenzo-21-crown-7; heptabenzo-28-crown-7; and heptabenzo-35-crown-7.

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O Valence Stabilizer #17e: Examples of eight-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of oxygen (usually ester or hydroxyl groups) and are not contained in component heterocyclic rings (O-O Bidentates, O-O Tridentates, O-O Tetridentates, and O-O Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 16-crown-8; 24-crown-8; 32-crown-8; 40-crown-8; 48-crown-8; tetrabenzo-16-crown-8; tetrabenzo-24-crown-8; tetrabenzo-32-crown-8; tetrabenzo-40-crown-8; tetrabenzo-48-crown-8; octabenzo-16-crown-8; octabenzo-24-crown-8; octabenzo-32-crown-8;

octabenzo-40-crown-8; and octabenzo-48-crown-8.

5 O Valence Stabilizer #17f: Examples of ten-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of oxygen (usually ester or hydroxyl groups) and are not contained in component heterocyclic rings (O-O Bidentates, O-O Tridentates, O-O Tetridentates, and O-O Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 20-crown-10; 30-crown-10; 40-crown-10; 50-crown-10; pentabenz-20-crown-10; pentabenz-30-crown-10; pentabenz-40-crown-10; and pentabenz-10 50-crown-10.

15 O Valence Stabilizer #18: Examples of four-, five-, six-, seven-, eight-, and ten-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of oxygen and are contained in component 5-membered heterocyclic rings (O-O Bidentates, O-O Tridentates, O-O Tetridentates, and O-O Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: tetrafurans, tetrabenzofurans; pentafurans; pentabenzofurans; hexafurans; hexabenzofurans; heptafurans; heptabenzofurans; octafurans; octabenzofurans; decafurans; and decabenzofurans.

20 O Valence Stabilizer #19: Examples of four-, five-, six-, seven-, eight-, and ten-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of oxygen and are contained in component 6-membered heterocyclic rings (O-O Bidentates, O-O Tridentates, O-O Tetridentates, and O-O Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: tetrapyrans, tetrabenzopyrans; pentapyrans; pentabenzopyrans; hexapyrans; hexabenzopyrans; heptapyrans; heptabenzopyrans; octapyrans; octabenzopyrans; decapyrans; and decabenzopyrans.

25 N-S Valence Stabilizer #1: Examples of thioimidates, dithioimidates, polythioimidates, and derivatives of thioimidic acid (N-S bidentates and N-S tetridentates) that meet the requirements

for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: S-methyl formathioimidate; S-ethyl formathioimidate; S-methyl acetathioimidate; S-ethyl acetathioimidate; S-methyl benzthioimidate; S-ethyl benzthioimidate; S-methyl cyclohexylthioimidate; S-ethyl cyclohexylthioimidate; S-methyl pentafluorobenzthioimidate; S-ethyl pentafluorobenzthioimidate; S-methyl 2-pyridylthioimidate; S-ethyl 2-pyridylthioimidate; S,S'-dimethyl benzodithioimidate; S,S'-dimethyl tetrafluorobenzdithioimidate; 2-iminothiolane; and 2-iminotetrahydrothiopyran. [Note: many thioimidate complexes are decomposed by water, but their stability can be enhanced through the use of fluorinated solubility control anions (e.g., PF₆⁻).]

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N-S Valence Stabilizer #2: Examples of thioguanylureas, guanidinothioureas, bis(thioguanylureas), bis(guanidinothioureas, poly(thioguanylureas), and poly(guanidinothioureas) (N-S Bidentates and N-S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: thioguanylurea (amidinothiourea); guanidinothiourea; methylthioguanylurea; ethylthioguanylurea; isopropylthioguanylurea; butylthioguanylurea; benzylthioguanylurea; phenylthioguanylurea; tolylthioguanylurea; naphthylthioguanylurea; cyclohexylthioguanylurea; norbornylthioguanylurea; adamantlylthioguanylurea; dimethylthioguanylurea; diethylthioguanylurea; diisopropylthioguanylurea; dibutylthioguanylurea; dibenzylthioguanylurea; diphenylthioguanylurea; ditolylthioguanylurea; dinaphthylthioguanylurea; dicyclohexylthioguanylurea; dinorbornylthioguanylurea; diadamantlylthioguanylurea; ethylenebis(thioguanylurea); propylenebis(thioguanylurea); phenylenebis(thioguanylurea); piperazinebis(thioguanylurea); oxalylbis(thioguanylurea); malonylbis(thioguanylurea); succinylbis(thioguanylurea); and phthalylbis(thioguanylurea).
25 [Note: thioguanylureas generally tend to favor lower oxidation states in complexed metals.]

N-S Valence Stabilizer #3: Examples of amidinothioamides, guanidinothioamides, bis(amidinothioamides), bis(guanidinothioamides), poly(amidinothioamides), and poly(guanidinothioamides) (including both N-amidinothioamides and 2-amidinothioacetamides) (N-S Bidentates, N-S Tridentates, and N-S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: amidinothioacetamide;

guanidinothioamide, amidinothiopropanamide; amidinothiobutanamide; amidinothiobenzamide; amidinothiotoluamide; amidinothiocyclohexamide; N-methylamidinothioacetamide; N-ethylamidinothiopropanamide; N-propylamidinothiobutanamide; N-phenylamidinothiobenzamide; N-tolylamidinothiotoluamide; N-
5 cyclohexylamidinothiocyclohexamide; bis(amidinothiooxamide); bis(amidinothiomalonamide); bis(amidinothiosuccinamide); bis(amidinothiophthalamide); 2-amidinothioacetamide (thiomalonamidine); N-methyl-2-amidinothioacetamide; N-ethyl-2-amidinothioacetamide; N-phenyl-2-amidinothioacetamide; N-benzyl-2-amidinothioacetamide; N-cyclohexyl-2-amidinothioacetamide; N,N'-dimethyl-2-amidinothioacetamide; N,N'-diethyl-2-
10 amidinothioacetamide; N,N'-diphenyl-2-amidinothioacetamide; N,N'-dibenzyl-2-amidinothioacetamide; and N,N'-dicyclohexyl-2-amidinothioacetamide. [Note: amidinothioamides generally tend to favor lower oxidation states in complexed metals.]

N-S Valence Stabilizer #4: Examples of imidoylthioamides, bis(imidoylthioamides), and poly(imidoylthioamides) (N-S Bidentates, N-S Tridentates, and N-S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: acetimidoylthioacetamide; acetimidoylthiopropanamide; acetimidoylthiobutanamide; acetimidoylthiobenzamide; acetimidoylthiotoluamide; acetimidoylthiocyclohexamide; propimidoylthiopropanamide; butimidoylthiobutanamide; benzimidoylthiobenzamide; ethylenebis(acetimidoylthioacetamide); propylenebis(acetimidoylthioacetamide); and phenylenebis(acetimidoylthioacetamide). [Note: imidoylthioamides generally tend to favor lower oxidation states in complexed metals.]

N-S Valence Stabilizer #5: Examples of thioureas, bis(thioureas), and poly(thioureas), including thiourylene complexes (N-S bidentates and N-S tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: thiourea; methylthiourea; ethylthiourea; isopropylthiourea; benzylthiourea; phenylthiourea; cyclohexylthiourea; naphthylthiourea (ntu); biphenylthiourea; norbornylthiourea; adamantlylthiourea; N,N'-dimethylthiourea; N,N'-diethylthiourea; N,N'-diisopropylthiourea; N,N'-dibenzylthiourea; N,N'-dicyclohexylthiourea; N,N'-dinaphthylthiourea; N,N'-
25 dibiphenylthiourea; N,N'-dinorbornylthiourea; N,N'-diadamantlylthiourea; tetramethylthiourea;
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ethylenethiourea (2-imidazolidinethione)(etu); 4,5-dihydroxy-2-imidazolinethione (dhetu); propylenethiourea; N-(thiazol-2-yl)thiourea; diphenylphosphinothioyl thioureas; allylthiourea; N-allyl-N'-pyridylthiourea; N-allyl-N'-anisylthiourea; N-allyl-N'-naphthylthiourea; N-allyl-N'-phenylthiourea; thioglycoluril (acetylenethiourea); and bis(pyridylmethyl)thiourea. [Note: 5 thioureas generally tend to favor lower oxidation states in complexed metals.]

N-S Valence Stabilizer #6: Examples of thiocarboxamides, bis(thiocarboxamides), and poly(thiocarboxamides), (N-S bidentates, N-S tridentates, and N-S tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 10 thiocarbamide (tu); thioacetamide (taa); thiopropionamide; thiobutanamide; thiobenzamide (1-phenylthioformamide)(tba); 1-naphthylthioformamide; 1-cyclohexylthioformamide); 1-norbornylthioformamide; 1-adamantylthioformamide; N,N-dimethylthioformamide; N,N-dimethylthioacetamide; pyridine-2-thiocarboxamide (thiopicolinamide); pyrazine-2,3-dithiocarboxamide; thionicotinamide; 2-thiophenethiocarboxamide; N,N-dimethylthiobenzamide; N-ethylthiocarbamide (N-etu); tetramethylthiocarbamide (tmtu); 2-thioacetamidothiazole (tatz); and polythioacrylamides. [Note: thiocarboxamides generally tend to favor lower oxidation states in complexed metals.]

N-S Valence Stabilizer #7: Examples of imidosulfurous diamides and bis(imidosulfurous 20 diamides) (N-S Bidentates, N-S Tridentates, and N-S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: N,N'-diphenylimidosulfurous diamide; N,N'-dibenzylimidosulfurous diamide; and phenylenebis(imidosulfurous diamide). [Note: these complexes tend to hydrolyze unless stabilized with a fluorinated anionic solubility control agent. The sulfite (S⁺⁴) valence of the 25 sulfur atom makes stabilization of high valence metal ions much more difficult, though still possible.]

N-S Valence Stabilizer #8: Examples of sulfurdiiamines, bis(sulfurdiiamines), and poly(sulfurdiiamines) (N-S Bidentates, N-S Tridentates, and N-S Tetridentates) that meet the 30 requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: N,N'-diphenylsulfurdiiimine; N,N'-dibenzylsulfurdiiimine; and phenylenebis(sulfurdiiimine).

[Note: these complexes tend to hydrolyze unless stabilized with a fluorinated anionic solubility control agent. The sulfite (S^{+4}) valence of the sulfur atom makes stabilization of high valence metal ions much more difficult, though still possible.]

- 5 N-S Valence Stabilizer #9: Examples of phosphonimidothioic acid, phosphonimidodithioic acid, bis(phosphonimidothioic acid); bis(phosphonimidodithioic acid), and derivatives thereof (N-S Bidentates, N-S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce^{+4} include, but are not limited to: phosphonimidothioic acid, phosphonimidodithioic acid; O-phenylphosphonimidothioic acid; O-benzylphosphonimidothioic acid; O-cyclohexylphosphonimidothioic acid; O-norbornylphosphonimidothioic acid; S-phenylphosphonimidodithioic acid; S-benzylphosphonimidodithioic acid; S-cyclohexylphosphonimidodithioic acid; and S-norbornylphosphonimidodithioic acid. [Note: the phosphite (P^{+3}) valence of the phosphorus atom makes stabilization of high valence metal ions much more difficult, though still possible.]
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- 15 N-S Valence Stabilizer #10: Examples of phosphonothioic diamides, bis(phosphonothioic diamides), and poly(phosphonothioic diamides) (N-S Bidentates and N-S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce^{+4} include, but are not limited to: phosphonothioic diamide, phosphonothioic dihydrazide, phosphonamidothioic hydrazide, N-phenylphosphonothioic diamide, N-benzylphosphonothioic diamide, N-cyclohexylphosphonothioic diamide, and N-norbornylphosphonothioic diamide. [Note: the phosphite (P^{+3}) valence of the phosphorus atom makes stabilization of high valence metal ions much more difficult, though still possible.]
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- 25 N-S Valence Stabilizer #11: Examples of phosphonamidothioic acid, phosphonamidimidodithioic acid, bis(phosphonamidothioic acid), bis(phosphonamidimidodithioic acid), poly(phosphonamidothioic acid), and poly(phosphonamidimidodithioic acid), and derivatives thereof (N-S Bidentates and N-S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce^{+4} include, but are not limited to: phosphonamidothioic acid, phosphonamidimidodithioic acid, phosphonohydrazidodithioic acid, phosphonohydrazidothioic acid, S-
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phenylphosphonamidimidodithioic acid, S-benzylphosphonamidimidodithioic acid, S-cyclohexylphosphonamidimidodithioic acid, and S-norbornylphosphonamidimidodithioic acid. [Note: the phosphite (P^{+3}) valence of the phosphorus atom makes stabilization of high valence metal ions much more difficult, though still possible.]

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N-S Valence Stabilizer #12: Examples of beta-aminothiones (N-substituted 3-amino-2-propenethioaldehydes), bis(beta-aminothiones), and poly(beta-aminothiones) (N-S Bidentates and N-S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce^{+4} include, but are not limited to: 4-methylamino-3-penten-2-thione; 4-ethylamino-3-penten-2-thione; 4-isopropylamino-3-penten-2-thione; 4-phenylamino-3-penten-2-thione; 4-naphthylamino-3-penten-2-thione; 4-cyclohexylamino-3-penten-2-thione; 4-norbornylamino-3-penten-2-thione; 4-hydroxyamino-3-penten-2-thione; 3-methylamino-1-phenyl-2-butenethioaldehydel; 3-ethylamino-1-phenyl-2-butenethioaldehyde; 3-isopropylamino-1-phenyl-2-butenethioaldehyde; 3-phenylamino-1-phenyl-2-butenethioaldehyde; 3-naphthylamino-1-phenyl-2-butenethioaldehyde; 3-cyclohexylamino-1-phenyl-2-butenethioaldehyde; 3-norbornylamino-1-phenyl-2-butenethioaldehyde; 3-hydroxyamino-1-phenyl-2-butenethioaldehyde; 3-phenylamino-1,3-diphenyl-2-propenethioaldehyde; 3-cyclohexylamino-1,3-dicyclohexyl-2-propenethioaldehyde; and 3-norbornylamino-1,3-dinorbornyl-2-propenethioaldehyde.

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N-S Valence Stabilizer #13: Examples of 3-aminothioacrylamides (3-amino-2-thiopropenamides), 3,3-diaminothioacrylamides, bis(3-aminothioacrylamides), bis(3,3-diaminothioacrylamides), poly(3-aminothioacrylamides), and poly(3,3-diaminothioacrylamides) (N-S Bidentates and N-S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce^{+4} include, but are not limited to: 3-methylaminothioacrylamide; 3-ethylaminothioacrylamide, 3-isopropylaminothioacrylamide, 3-phenylaminothioacrylamide; 3-naphthylaminothioacrylamide; 3-cyclohexylaminothioacrylamide; 3-norbornylaminothioacrylamide; 3-hydroxyaminothioacrylamide; N-methyl-3-methylaminothioacrylamide; N-ethyl-3-ethylaminothioacrylamide, N-isopropyl-3-isopropylaminothioacrylamide, N-phenyl-3-phenylaminothioacrylamide; N-naphthyl-3-naphthylaminothioacrylamide; N-cyclohexyl-3-cyclohexylaminothioacrylamide; N-norbornyl-3-

norbornylaminothioacrylamide; 3-amino-3-methylaminothioacrylamide; 3-amino-3-ethylaminothioacrylamide, 3-amino-3-isopropylaminothioacrylamide, 3-amino-3-phenylaminothioacrylamide; 3-amino-3-naphthylaminothioacrylamide; 3-amino-3-cyclohexylaminothioacrylamide; 3-amino-3-norbornylaminothioacrylamide; and 3-amino-3-hydroxyaminothioacrylamide.

N-S Valence Stabilizer #14: Examples of 3-aminothioacrylic acids (3-amino-2-thiopropenoic acids), 3-mercaptopropanoic acids, bis(3-aminothioacrylic acids), bis(3-mercaptopropanoic acids), poly(3-aminothioacrylic acids), and poly(3-mercaptopropanoic acids), and derivatives thereof (N-S Bidentates and N-S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 3-aminothioacrylic acid; 3-mercaptopropanoic acid; 3-methylaminothioacrylic acid; 3-ethylaminothioacrylic acid; 3-isopropylaminothioacrylic acid; 3-phenylaminothioacrylic acid; 3-naphthylaminothioacrylic acid; 3-cyclohexylaminothioacrylic acid; 3-norbornylaminothioacrylic acid; 3-hydroxyaminothioacrylic acid; methyl 3-methylaminothioacrylate; ethyl 3-ethylaminothioacrylate; isopropyl 3-isopropylaminothioacrylate; benzyl 3-phenylaminothioacrylate; naphthyl 3-naphthylaminothioacrylate; cyclohexyl 3-cyclohexylaminothioacrylate; and norbornyl 3-norbornylaminothioacrylate.

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N-S Valence Stabilizer #15: Examples of N-thioacyl benzylidenimines, bis(N-thioacyl benzylidenimines), and poly(N-thioacyl benzylidenimines) (N-S Bidentates and N-S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: N-thioformyl benzylidenimine, N-thioacetyl benzylidenimine; N-thiobenzoyl benzylidenimine; and N-pentafluorothiobenzoyl benzylidenimine.

N-S Valence Stabilizer #16: Examples of thiocarbonyl oximes, bis(thiocarbonyl oximes), and poly(thiocarbonyl oximes) (N-S Bidentates, N-S Tridentates, and N-S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: butane-3-thione-2-one monoxime); and diphenylethane-2-thione-1-one monoxime.

N-S Valence Stabilizer #17: Examples of mercapto oximes, bis(mercapto oximes), and poly(mercapto oximes) (including 2-sulfur heterocyclic oximes) (N-S Bidentates, N-S Tridentates, N-S Tetridentates, and N-S Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 3-mercaptoputan-2-one oxime; 4-mercaptophexan-3-one oxime; (1,2-diphenyl-2-mercptoethanone oxime); 1,2-di(trifluoromethyl)-2-mercptoethanone oxime; 1,2-dicyclohexyl-2-mercptoethanone oxime; 1,2-dinorbornyl-2-mercptoethanone oxime; 2-mercaptobenzaldehyde oxime; 2-mercpto-1-naphthaldehyde oxime; thiophene-2-aldoxime; methyl 2-thiophenyl ketoxime; and phenyl 2-thiophenyl ketoxime.

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N-S Valence Stabilizer #18: Examples of 2-nitrothiophenols (2-nitrobenzenethiols) (N-S Bidentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-nitrothiophenol; 2,3-dinitrothiophenol; 2,4-dinitrothiophenol; 2,5-dinitrothiophenol; 2,6-dinitrothiophenol; 1-nitro-2-naphthalenethiol; and 2-nitro-1-naphthalenethiol.

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N-S Valence Stabilizer #19: Examples of 2-nitrlothiophenols (2-nitrilobenzeneithiols) (N-S Bidentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-cyanothiophenol; 2,3-dicyanothiophenol; 2,4-dicyanothiophenol; 2,5-dicyanothiophenol; 2,6-dicyanothiophenol; 1-cyano-2-naphthalenethiol; and 2-cyano-1-naphthalenethiol.

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N-S Valence Stabilizer #20: Examples of thiohydrazides, bis(thiohydrazides), and poly(thiohydrazides) (N-S Bidentates and N-S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: thioformic hydrazide; thioacetic hydrazide; thiopropionic hydrazide; thiobenzoic hydrazide; thiophthalhydrazide; thiosalicylic hydrazide; thionaphthoic hydrazides; thionorbornaneacetic hydrazide; thionicotinic hydrazide; and thioisonicotinic hydrazide. [Note: thiohydrazides prefer complexation with lower oxidation states in metal ions.]

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N-S Valence Stabilizer #21: Examples of thiosemicarbazides, bis(thiosemicarbazides), and poly(thiosemicarbazides) (N-S Bidentates, N-S Tetridentates, and N-S Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: thiosemicarbazide (tsc); thiosemicarbazide diacetic acid (tsda); 1-methylthiosemicarbazide (1mts); 1-ethylthiosemicarbazide; 1-isopropylthiosemicarbazide; 1-phenylthiosemicarbazide (1pts)(cryogenine); 1-benzylthiosemicarbazide; 1-cyclohexylthiosemicarbazide; 1-norbornylthiosemicarbazide; 4-methylthiosemicarbazide (4mts); 4-ethylthiosemicarbazide; 4-isopropylthiosemicarbazide; 4-phenylthiosemicarbazide (4-pts); 4-benzylthiosemicarbazide; 4-cyclohexylthiosemicarbazide; 4-norbornylthiosemicarbazide; 10 nicotinic thiosemicarbazide; isonicotinic thiosemicarbazide; and 4-phenyl-1-benzenesulfonyl-3-thiosemicarbazide (pbst). [Note: thiosemicarbazides prefer complexation with lower oxidation states in metal ions.]

N-S Valence Stabilizer #22: Examples of five-, seven-, or nine-membered macrocyclics, 15 macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of nitrogen (usually amine or imine groups) or sulfur (usually thiols, mercaptans, or thiocarbonyls) and are not contained in component heterocyclic rings (N-S Tridentates, N-S Tetridentates, and N-S Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 20 triazadithiacyclodecane ([10]aneS₂N₃); triazadithiacycloundecane ([11]aneS₂N₃); triazadithiacyclododecane ([12]aneS₂N₃); triazadithiacyclotridecane ([13]aneS₂N₃); triazadithiacyclotetradecane ([14]aneS₂N₃); triazadithiacyclopentadecane ([15]aneS₂N₃); thiomorpholine; and thiazolidine.

25 N-S Valence Stabilizer #23: Examples of five- or seven-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of nitrogen or sulfur and are contained in component heterocyclic rings (N-S Bidentates, N-S Tridentates, N-S Tetridentates, or N-S Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ 30 include, but are not limited to: dithiopyrantripyridines; dithiophenetripyrroles; trithiopyrantetrapyridines; and trithiophenetetrapyrroles.

N-S Valence Stabilizer #24: Examples of five-, seven-, or nine-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of nitrogen or sulfur and are contained in a combination of heterocyclic rings and amine, imine, thiol, mercapto, or thiocarbonyl groups (N-S Bidentates, N-S Tridentates, N-S Tetridentates, or N-S Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: azathiapentaphyrins; diazadithiapentaphyrins; azathiapentaphyrins; and diazadithiapentaphyrins.

N-O Valence Stabilizer #1: Examples of imides, diimides, polyimides, and derivatives of imidic acid (N-O bidentates and N-O tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: O-methyl formimidate; O-ethyl formimidate; O-methyl acetimidate; O-ethyl acetimidate; O-methyl benzimidate; O-ethyl benzimidate; O-methyl cyclohexylimide; O-ethyl cyclohexylimide; O-methyl pentafluorobenzimidate; O-ethyl pentafluorobenzimidate; O-methyl 2-pyridylimide; O-ethyl 2-pyridylimide; O,O'-dimethyl benzdiimide; O,O'-dimethyl tetrafluorobenzdiimide; 2-iminotetrahydrofuran; and 2-iminotetrahydropyran. [Note: most imide complexes are decomposed by water, but their stability can be enhanced through the use of fluorinated solubility control anions (e.g. PF₆⁻).]

N-O Valence Stabilizer #2: Examples of pseudoureas, bis(pseudoureas), and poly(pseudoureas) (N-O bidentates and N-O tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: O-methyl pseudourea; O-ethyl pseudourea; O-isopropyl pseudourea; O-benzyl pseudourea; O-cyclohexyl pseudourea; O-norbornyl pseudourea; O-pentafluorobenzyl pseudourea; N-methyl pseudourea; N-ethyl pseudourea; N-isopropyl pseudourea; N-benzyl pseudourea; N-cyclohexyl pseudourea; N-norbornyl pseudourea; and N-pentafluorobenzyl pseudourea.

N-O Valence Stabilizer #3: Examples of 2-amidinoacetates, bis(2-amidinoacetates), and poly(2-amidinoacetates) (N-O Bidentates and N-O Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: N-methyl-2-amidinoacetate; O-methyl-2-amidinoacetate; N-benzyl-2-amidinoacetate; and O-benzyl-2-

amidinoacetate. [Note: many 2-amidinoacetates tend to hydrolyze in water. This can be minimized through the use of fluorinated solubility control anions such as PF_6^- .]

N-O Valence Stabilizer #4: Examples of ureas, bis(ureas), and poly(ureas), including urylene complexes (N-O bidentates and N-O tetradentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce^{+4} include, but are not limited to: urea; methylurea; ethylurea; isopropylurea; benzylurea; cyclohexylurea; naphthylurea; biphenylurea; norbornylurea; adamantlylurea; N,N'-dimethylurea; N,N'-diethylurea; N,N'-diisopropylurea; N,N'-dibenzylurea; N,N'-dicyclohexylurea; N,N'-dinaphthylurea; N,N'-dibiphenylurea; N,N'-dinorbornylurea; N,N'-diadamantlylurea; ethyleneurea (2-imidazolidone); propyleneurea; glycoluril (acetyleneurea); and N,N'-bis(4-nitrophenyl)urea.

N-O Valence Stabilizer #5: Examples of phosphonimidic acid, bis(phosphonimidic acid), poly(phosphonimidic acid), and derivatives thereof (N-O Bidentates and N-O Tetradentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce^{+4} include, but are not limited to: phosphonimidic acid; O-phenylphosphonimidic acid; O-benzylphosphonimidic acid; O-cyclohexylphosphonimidic acid; and O-norbornylphosphonimidic acid. [Note: the phosphite (P^{+3}) valence of the phosphorus atom makes stabilization of high valence metal ions much more difficult, though still possible.]

N-O Valence Stabilizer #6: Examples of phosphonamidic acid, phosphonic diamide, bis(phosphonamidic acid), bis(phosphonic diamide), poly(phosphonamidic acid), poly(phosphonic diamide), and derivatives thereof (N-O Bidentates and N-O Tetradentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce^{+4} include, but are not limited to: phosphonamidic acid, phosphonic diamide, phosphonamidic hydrazide, phosphonic dihydrazide, O-phenylphosphonamidic acid, O-benzylphosphonamidic acid, O-cyclohexylphosphonamidic acid, O-norbornylphosphonamidic acid, N-benzylphosphonic diamide, N-phenylphosphonic diamide, N-cyclohexylphosphonic diamide, and N-norbornylphosphonic diamide. [Note: the phosphite (P^{+3}) valence of the phosphorus atom makes stabilization of high valence metal ions much more difficult, though still possible.]

N-O Valence Stabilizer #7: Examples of beta-ketoamines (N-substituted 3-amino-2-propenals), bis(beta-ketoamines), and poly(beta-ketoamines) (N-O Bidentates and N-O Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 4-methylamino-3-penten-2-one; 4-ethylamino-3-penten-2-one; 4-isopropylamino-3-penten-2-one; 4-phenylamino-3-penten-2-one; 4-naphthylamino-3-penten-2-one; 4-cyclohexylamino-3-penten-2-one; 4-norbornylamino-3-penten-2-one; 4-hydroxyamino-3-penten-2-one; 3-methylamino-1-phenyl-2-butenal; 3-ethylamino-1-phenyl-2-butenal; 3-isopropylamino-1-phenyl-2-butenal; 3-phenylamino-1-phenyl-2-butenal; 3-naphthylamino-1-phenyl-2-butenal; 3-cyclohexylamino-1-phenyl-2-butenal; 3-norbornylamino-1-phenyl-2-butenal; 3-hydroxyamino-1-phenyl-2-butenal; 3-phenylamino-1,3-diphenyl-2-propenal; 3-cyclohexylamino-1,3-dicyclohexyl-2-propenal; 3-norbornylamino-1,3-dinorbornyl-2-propenal; 2,2'-pyridil; alpha-pyridoin; 4-aminoantipyrine (aap); beta-phenylaminopropiophenone; and polyaminoquinones (PAQs).

N-O Valence Stabilizer #8: Examples of 3-aminoacrylamides (3-amino-2-propenamides), 3,3-diaminoacrylamides, bis(3-aminoacrylamides), bis(3,3-diaminoacrylamides), poly(3-aminoacrylamides), and poly(3,3-diaminoacrylamides) (N-O Bidentates and N-O Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 3-methylaminoacrylamide; 3-ethylaminoacrylamide, 3-isopropylaminoacrylamide, 3-phenylaminoacrylamide; 3-naphthylaminoacrylamide; 3-cyclohexylaminoacrylamide; 3-norbornylaminoacrylamide; 3-hydroxyaminoacrylamide; N-methyl-3-methylaminoacrylamide; N-ethyl-3-ethylaminoacrylamide, N-isopropyl-3-isopropylaminoacrylamide, N-phenyl-3-phenylaminoacrylamide; N-naphthyl-3-naphthylaminoacrylamide; N-cyclohexyl-3-cyclohexylaminoacrylamide; N-norbornyl-3-norbornylaminoacrylamide; 3-amino-3-methylaminoacrylamide; 3-amino-3-ethylaminoacrylamide, 3-amino-3-isopropylaminoacrylamide, 3-amino-3-phenylaminoacrylamide; 3-amino-3-naphthylaminoacrylamide; 3-amino-3-cyclohexylaminoacrylamide; 3-amino-3-norbornylaminoacrylamide; and 3-amino-3-hydroxyaminoacrylamide.

N-O Valence Stabilizer #9: Examples of 3-aminoacrylic acids (3-amino-2-propenoic acids), 3-hydroxy-3-aminoacrylic acids, bis(3-aminoacrylic acids), bis(3-hydroxy-3-aminoacrylic acids), poly(3-aminoacrylic acids), and poly(3-hydroxy-3-aminoacrylic acids), and derivatives thereof (N-O Bidentates and N-O Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 3-aminoacrylic acid; 3-hydroxy-3-aminoacrylic acid; 3-methylaminoacrylic acid; 3-ethylaminoacrylic acid; 3-isopropylaminoacrylic acid; 3-phenylaminoacrylic acid; 3-naphthylaminoacrylic acid; 3-cyclohexylaminoacrylic acid; 3-norbornylaminoacrylic acid; 3-hydroxyaminoacrylic acid; methyl 3-methylaminoacrylate; ethyl 3-ethylaminoacrylate; isopropyl 3-isopropylaminoacrylate; benzyl 3-phenylaminoacrylate; naphthyl 3-naphthylaminoacrylate; cyclohexyl 3-cyclohexylaminoacrylate; and norbornyl 3-norbornylaminoacrylate.

N-O Valence Stabilizer #10: Examples of N-acyl benzylidenimines, bis(N-acyl benzylidenimines), and poly(N-acyl benzylidenimines) (N-O Bidentates and N-O Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: N-formyl benzylidenimine, N-acetyl benzylidenimine; N-benzoyl benzylidenimine; and N-pentafluorobenzoyl benzylidenimine.

N-O Valence Stabilizer #11: Examples of 2-nitroanilines (N-O Bidentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-nitroaniline; 2,6-dintroaniline; 2-nitrophenylenediamine; 2-nitrophenylenetriamine; 2-nitro-1-aminonaphthalene; 1-nitro-2-aminonaphthalene; nitrodiaminonaphthalene; and dipicrylamine.

N-O Valence Stabilizer #12: Examples of 2-nitrilophenols (N-O Bidentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-cyanophenol; 2,3-dicyanophenol; 2,4-dicyanophenol; 2,5-dicyanophenol; 2,6-dicyanophenol; 1-cyano-2-naphthol; and 2-cyano-1-naphthol. Also includes acylcyanamides.

N-O Valence Stabilizer #13: Examples of amine N-oxides and N-diazine oxides (azoxy compounds) (N-O Bidentates, N-O Tridentates, and N-O Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to:

pyridine N-oxide (pyNO or PNO); picoline N-oxide (picNO); lutidine N-oxide (lutNO or LNO);
collidine N-oxide (collNO or CNO); quinoline N-oxide (QuinNO or QNO); isoquinoline N-
oxide (isoQuinNO or IQNO); acridine N-oxide (AcrNO or ANO); picolinic acid N-oxide
(PicANO); pyridinethiolate N-oxide (PTNO); adenine N-oxide; adenosine N-oxide; 1,10-
5 phenanthroline mono-N-oxide (phenNO); 1,10-phenanthroline N,N-dioxide (phen2NO);
bipyridyl mono-N-oxide (bipyNO); bipyridyl N,N-dioxide (bipy2NO); pyrazine mono-N-oxide
(pyzNO); pyrazine N,N-dioxide (pyz2NO); pyrimidine mono-N-oxide (pymNO); pyrimidine
N,N-dioxide (pym2NO); pyridazine mono-N-oxide (pdzNO); pyridazine N,N-dioxide (pdz2NO);
quinoxaline mono-N-oxide (qxNO); quinoxaline N,N-dioxide (qx2NO); phenazine mono-N-
10 oxide (phzNO); phenazine N,N-dioxide (phz2NO); 2,3-di(pyridine N-oxide)quinoxaline (dpoq);
inosine N-oxide; 4,4'-bipyridine N,N-dioxide; 1-hydroxypyrazole 2-oxide; 1-hydroxyimidazole
3-oxide; 2,2'-diimidazyl 3,3'-dioxide; imidazole N-oxides (1-hydroxyimidazole-3-N-oxides); N-
benzylidene aniline N-oxide; N-(naphthylidene) aniline N-oxide; N-(hydroxybenzylidene) aniline
N-oxide; and 2,2'-dibenzimidazyl 3,3'-dioxide (indigo N,N-dioxide) for amine N-oxides; and
15 azoxybenzene; phthalazine N-oxide; benzocinnoline N-oxide; and bipyrazinyl N-oxide as N-
diazine oxide examples.

20 N-O Valence Stabilizer #14: Examples of hydrazides, bis(hydrazides), and poly(hydrazides) (N-
O Bidentates and N-O Tetridentates) that meet the requirements for use as “narrow band”
valence stabilizers for Ce⁺⁴ include, but are not limited to: formic hydrazide; acetic hydrazide;
propionic hydrazide; benzoic hydrazide; phthalhydrazide; salicylic hydrazide; naphthoic
hydrazides; norbornaneacetic hydrazide; nicotinic hydrazide; and isonicotinic hydrazide
(isoniazid). [Note: hydrazides prefer complexation with lower oxidation states in metal ions.]

25 N-O Valence Stabilizer #15: Examples of semicarbazides, bis(semicarbazides), and
poly(semicarbazides) (N-O Bidentates, N-O Tetridentates, and N-O Hexadentates) that meet the
requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to:
semicarbazide (sc); semicarbazide diacetic acid (sda); 1-methylsemicarbazide; 1-
ethylsemicarbazide; 1-isopropylsemicarbazide; 1-phenylsemicarbazide; 1-benzylsemicarbazide;
30 1-cyclohexylsemicarbazide; 1-norbornylsemicarbazide; 4-methylsemicarbazide; 4-
ethylsemicarbazide; 4-isopropylsemicarbazide; 4-phenylsemicarbazide; 4-benzylsemicarbazide;

4-cyclohexylsemicarbazide; 4-norbornylsemicarbazide; nicotinic semicarbazide; and isonicotinic semicarbazide. [Note: semicarbazides prefer complexation with lower oxidation states in metal ions.]

5 N-O Valence Stabilizer #16: Examples of five-, seven-, or nine-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of nitrogen (usually amine or imine groups) or oxygen (usually hydroxy, carboxy, or carbonyl groups) and are not contained in component heterocyclic rings (N-O Tridentates, N-O Tetridentates, and N-O Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to:

10 triazadioxacyclodecane ([10]aneO₂N₃); triazadioxacycloundecane ([11]aneO₂N₃); triazadioxacyclododecane ([12]aneO₂N₃); triazadioxacyclotridecane ([13]aneO₂N₃); triazadioxacyclotetradecane ([14]aneO₂N₃); and triazadioxacyclopentadecane ([15]aneO₂N₃).

15 N-O Valence Stabilizer #17: Examples of five- or seven-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of nitrogen or oxygen and are contained in component heterocyclic rings (N-O Bidentates, N-O Tridentates, N-O Tetridentates, or N-O Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dipyrantripyridines; difurantripyrroles; tripyrantetrapyridines; and trifurantetrapyrroles.

20 N-O Valence Stabilizer #18: Examples of five-, seven-, or nine-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of nitrogen or oxygen and are contained in a combination of heterocyclic rings and amine, imine, hydroxy, carboxy, or carbonyl groups (N-O Bidentates, N-O Tridentates, N-O Tetridentates, or N-O Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: azaoxapentaphyrins; diazadioxapentaphyrins; azaoxapentaphyrins; and diazadioxapentaphyrins.

S-O Valence Stabilizer #1: Examples of thiobiurets (thioimidodicarbonic diamides), thioisobiurets, thiobiureas, thiotriurets, thiotriureas, bis(thiobiurets), bis(thioisobiurets), bis(thiobiureas), poly(thiobiurets), poly(thioisobiurets), and poly(thiobiureas) (S-O Bidentates, S-O Tridentates, S-O Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: thiobiuret, thioisobiuret, thiobiurea, thiotriuret, thiotriurea, nitrothiobiuret, dinitrothiobiuret, aminothiobiuret, diaminothiobiuret, oxythiobiuret, dioxythiobiuret, cyanothiobiuret, methylthiobiuret, ethylthiobiuret, isopropylthiobiuret, phenylthiobiuret, benzylthiobiuret, cyclohexylthiobiuret, norbornylthiobiuret, adamantlylthiobiuret, dimethylthiobiuret, diethylthiobiuret, diisopropylthiobiuret, diphenylthiobiuret, dibenzylthiobiuret, dicyclohexylthiobiuret, dinorbornylthiobiuret, diadamantlylthiobiuret’ and 3-formamidino thiocarbamides.

S-O Valence Stabilizer #2: Examples of acylthioureas, aroylthioureas, thioacylureas, thioaroylureas, bis(acylthioureas), bis(aroylthioureas), bis(thioacylureas), bis(thioaroylureas), poly(thioacylthioureas), poly(thioaroylthioureas), poly(thioacylureas), and poly(thioaroylureas) (S-O Bidentates, S-O Tridentates, S-O Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: thioformylurea, thioacetylurea, thiobenzoylurea, thiocyclohexoxylurea, pentafluorothiobenzoylurea, acetylthiourea, benzoylthiourea, and cyclohexoxylthiourea.

S-O Valence Stabilizer #3: Examples of thioimidodialdehydes, thiohydrazidodialdehydes (thioacyl hydrazides), bis(thioimidodialdehydes), bis(thiohydrazidodialdehydes), poly(thioimidodialdehydes), and poly(thiohydrazidodialdehydes) (S-O Bidentates, S-O Tridentates, S-O Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: thiodiacetamide, thiodipropanamide, thiodibutanamide, thiodibenzamide, and thiodicyclohexamide.

S-O Valence Stabilizer #4: Examples of thioimidodicarbonic acids, thiohydrazidodicarbonic acids, bis(thioimidodicarbonic acids), bis(thiohydrazidodicarbonic acids), poly(thioimidodicarbonic acids), poly(thiohydrazidodicarbonic acids) and derivatives thereof (S-O Bidentates, S-O Tridentates, S-O Tetridentates) that meet the requirements for use as “narrow

band" valence stabilizers for Ce⁺⁴ include, but are not limited to: thioimidodicarbonic acid, thiohydrazidodicarbonic acid, O-phenylthioimidodicarbonic acid, O-benzylthioimidodicarbonic acid, O-cyclohexylthioimidodicarbonic acid, O-norbornylthioimidodicarbonic acid, O,O'-diphenylthioimidodicarbonic acid, O,O'-dibenzylthioimidodicarbonic acid, O,O'-dicyclohexylthioimidodicarbonic acid, O,O'-dinorbornylthioimidodicarbonic acid.

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S-O Valence Stabilizer #5: Examples of 1,2-monothioketones (monothiolenes, monothio-alpha-ketonates), 1,2,3-monothioketones, 1,2,3-dithioketones, monothiotropolonates, ortho-monothioquinones, bis(1,2-monothioketones), and poly(1,2-monothioketones) (S-O Bidentates, S-O Tridentates, S-O Tetridentates) that meet the requirements for use as "narrow band" valence stabilizers for Ce⁺⁴ include, but are not limited to: monothiotropolone; 1,2-monothiobenzoquinone (o-monothioquinone); di-tert-butyl-1,2-monothiobenzoquinone; hexafluoro-1,2-monothiobenzoquinone; 1,2-monothionaphthoquinone; 9,10-monothiophenanthroquinone; monothiosquaric acid; monothiodeltic acid; monothiocroconic acid; and monothiorhodizonic acid.

S-O Valence Stabilizer #6: Examples of trithioperoxydicarbonic diamides, bis(trithioperoxydicarbonic diamides), and poly(trithioperoxydicarbonic diamides) (S-O Bidentates, S-O Tridentates, S-O Tetridentates) that meet the requirements for use as "narrow band" valence stabilizers for Ce⁺⁴ include, but are not limited to: trithioperoxydicarbonic diamide; N-phenyltrithioperoxydicarbonic diamide; N-benzyltrithioperoxydicarbonic diamide; N-cyclohexyltrithioperoxydicarbonic diamide; N-norbornyltrithioperoxydicarbonic diamide; N,N'-diphenyltrithioperoxydicarbonic diamide; N,N'-dibenzyltrithioperoxydicarbonic diamide; N,N'-dicyclohexyltrithioperoxydicarbonic diamide; and N,N'-dinorbornyltrithioperoxydicarbonic diamide.

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S-O Valence Stabilizer #7: Examples of dithiodicarbonic acids, bis(dithiodicarbonic acids), poly(dithiodicarbonic acids), and derivatives thereof (S-O Bidentates, S-O Tridentates, S-O Tetridentates) that meet the requirements for use as "narrow band" valence stabilizers for Ce⁺⁴ include, but are not limited to: dithiodicarbonic acid, O-phenyldithiodicarbonic acid, O-benzylidithiodicarbonic acid, O-cyclohexyldithiodicarbonic acid, O-norbornyldithiodicarbonic

acid, O,O'-diphenyldithiodicarbonic acid, O,O'-dibenzylidithiodicarbonic acid, O,O'-dicyclohexylidithiodicarbonic acid, and O,O'-dinorbornylidithiodicarbonic acid.

S-O Valence Stabilizer #8: Examples of trithioperoxydicarbonic acids,

5 bis(trithioperoxydicarbonic acids), poly(trithioperoxydicarbonic acids), and derivatives thereof (S-O Bidentates, S-O Tridentates, S-O Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to:
trithioperoxydicarbonic acid, O-phenyltrithioperoxydicarbonic acid; O-benzyltrithioperoxydicarbonic acid; O-cyclohexyltrithioperoxydicarbonic acid; O-norbornyltrithioperoxydicarbonic acid; O,O'-diphenyltrithioperoxydicarbonic acid; O,O'-dibenzyltrithioperoxydicarbonic acid; O,O'-dicyclohexyltrithioperoxydicarbonic acid; and O,O'-dinorbornyltrithioperoxydicarbonic acid.

S-O Valence Stabilizer #9: Examples of monothioperoxydiphosphoramides,

15 bis(monothioperoxydiphosphoramides), and poly(monothioperoxydiphosphoramides) (S-O Bidentates, S-O Tridentates, S-O Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to:
monothioperoxydiphosphoramide, N-methylmonothioperoxydiphosphoramide, N-isopropylmonothioperoxydiphosphoramide, N-tert-butylmonothioperoxydiphosphoramide, N-phenylmonothioperoxydiphosphoramide, N-pentafluorophenylmonothioperoxydiphosphoramide, N-benzylmonothioperoxydiphosphoramide, N-cyclohexylmonothioperoxydiphosphoramide, N-norbornylmonothioperoxydiphosphoramide, N,N''-dimethylmonothioperoxydiphosphoramide, N,N''-diisopropylmonothioperoxydiphosphoramide, N,N''-di-tert-butylmonothioperoxydiphosphoramide, N,N''-diphenylmonothioperoxydiphosphoramide,
20 N,N''-di-pentafluorophenylmonothioperoxydiphosphoramide, N,N''-dibenzylmonothioperoxydiphosphoramide, N,N''-dicyclohexylmonothioperoxydiphosphoramide, and N,N''-dinorbornylmonothioperoxydiphosphoramide.

30 S-O Valence Stabilizer #10: Examples of monothioperoxydiphosphoric acids,

bis(monothioperoxydiphosphoric acids), poly(monothioperoxydiphosphoric acids), and

derivatives thereof (S-O Bidentates, S-O Tridentates, S-O Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: monothioperoxydiphosphoric acid, methylmonothioperoxydiphosphoric acid, isopropylmonothioperoxydiphosphoric acid, tert-butylmonothioperoxydiphosphoric acid, phenylmonothioperoxydiphosphoric acid, pentafluorophenylmonothioperoxydiphosphoric acid, benzylmonothioperoxydiphosphoric acid, cyclohexylmonothioperoxydiphosphoric acid, norbornylmonothioperoxydiphosphoric acid, dimethylmonothioperoxydiphosphoric acid, diisopropylmonothioperoxydiphosphoric acid, di-tert-butylmonothioperoxydiphosphoric acid, diphenylmonothioperoxydiphosphoric acid, di-pentafluorophenylmonothioperoxydiphosphoric acid, dibenzylmonothioperoxydiphosphoric acid, dicyclohexylmonothioperoxydiphosphoric acid, and dinorbornylmonothioperoxydiphosphoric acid.

S-O Valence Stabilizer #11: Examples of monothioimidodiphosphonic acids, monothiohydrazidodiphosphonic acids, bis(monothioimidodiphosphonic acids), bis(monothiohydrazidodiphosphonic acids), poly(monothioimidodiphosphonic acids), poly(monothiohydrazidodiphosphonic acids), and derivatives thereof (S-O Bidentates, S-O Tridentates, S-O Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: monothioimidodiphosphonic acid, methylmonothioimidodiphosphonic acid, isopropylmonothioimidodiphosphonic acid, tert-butylmonothioimidodiphosphonic acid, phenylmonothioimidodiphosphonic acid, pentafluorophenylmonothioimidodiphosphonic acid, benzylmonothioimidodiphosphonic acid, cyclohexylmonothioimidodiphosphonic acid, norbornylmonothioimidodiphosphonic acid, dimethylmonothioimidodiphosphonic acid, diisopropylmonothioimidodiphosphonic acid, di-tert-butylmonothioimidodiphosphonic acid, diphenylmonothioimidodiphosphonic acid, di-pentafluorophenylmonothioimidodiphosphonic acid, dibenzylmonothioimidodiphosphonic acid, dicyclohexylmonothioimidodiphosphonic acid, and dinorbornylmonothioimidodiphosphonic acid. [Note: the phosphite (P⁺³) valence of the phosphorus atom makes stabilization of high valence metal ions much more difficult, though still possible.]

S-O Valence Stabilizer #12: Examples of monothioimidodiphosphonamides, monothiohydrazidodiphosphonamides, bis(monothioimidodiphosphonamides),

bis(monothiohydrazidodiphosphonamides), poly(monothioimidodiphosphonamides), and poly(monothiohydrazidodiphosphonamides) (S-O Bidentates, S-O Tridentates, S-O Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: monothioimidodiphosphonamide, N-

5 methylmonothioimidodiphosphonamide, N-isopropylmonothioimidodiphosphonamide, N-tert-butylmonothioimidodiphosphonamide, N-phenylmonothioimidodiphosphonamide, N-pentafluorophenylmonothioimidodiphosphonamide, N-benzylmonothioimidodiphosphonamide, N-cyclohexylmonothioimidodiphosphonamide, N-norbornylmonothioimidodiphosphonamide, N,N”-dimethylmonothioimidodiphosphonamide, N,N”-

10 diisopropylmonothioimidodiphosphonamide, N,N”-di-tert-butylmonothioimidodiphosphonamide, N,N”-diphenylmonothioimidodiphosphonamide, N,N”-di-pentafluorophenylmonothioimidodiphosphonamide, N,N”-dibenzylmonothioimidodiphosphonamide, N,N”-dicyclohexylmonothioimidodiphosphonamide, and N,N”-dinorbornylmonothioimidodiphosphonamide. [Note: the phosphite (P⁺³) valence of the phosphorus atom makes stabilization of high valence metal ions much more difficult, though still possible.]

S-O Valence Stabilizer #13: Examples of dithiodiphosphonamides, bis(dithiodiphosphonamides), and poly(dithiodiphosphonamides) (S-O Bidentates, S-O Tridentates, S-O Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dithiodiphosphonamide, N-methyldithiodiphosphonamide, N-isopropyldithiodiphosphonamide, N-tert-butyldithiodiphosphonamide, N-phenyldithiodiphosphonamide, N-pentafluorophenyldithiodiphosphonamide, N-benzyldithiodiphosphonamide, N-cyclohexyldithiodiphosphonamide, N-norbornyldithiodiphosphonamide, N,N”-dimethyldithiodiphosphonamide, N,N”-diisopropylidithiodiphosphonamide, N,N”-di-tert-butyldithiodiphosphonamide, N,N”-diphenyldithiodiphosphonamide, N,N”-dipentafluorophenyldithiodiphosphonamide, N,N”-dibenzylidithiodiphosphonamide, N,N”-dicyclohexyldithiodiphosphonamide, and N,N”-dinorbornyldithiodiphosphonamide. [Note: the phosphite (P⁺³) valence of the phosphorus atom makes stabilization of high valence metal ions much more difficult, though still possible.]

S-O Valence Stabilizer #14: Examples of dithiodiphosphonic acids, bis(dithiodiphosphonic acids), poly(dithiodiphosphonic acids), and derivatives thereof (S-O Bidentates, S-O Tridentates, S-O Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dithiodiphosphonic acid, methyldithiodiphosphonic acid, 5 isopropyldithiodiphosphonic acid, tert-butyldithiodiphosphonic acid, phenyldithiodiphosphonic acid, pentafluorophenyldithiodiphosphonic acid, benzylidithiodiphosphonic acid, cyclohexyldithiodiphosphonic acid, norbornyldithiodiphosphonic acid, dimethyldithiodiphosphonic acid, diisopropyldiothiodiphosphonic acid, di-tert-butylidithiodiphosphonic acid, diphenyldithiodiphosphonic acid, di-pentafluorophenyldithiodiphosphonic acid, dibenzylidithiodiphosphonic acid, dicyclohexyldithiodiphosphonic acid, and dinorbornyldithiodiphosphoric acid. [Note: the phosphite (P⁺³) valence of the phosphorus atom makes stabilization of high valence metal ions much more difficult, though still possible.]

S-O Valence Stabilizer #15: Examples of monothioperoxydiphosphonamides, bis(monothioperoxydiphosphonamides), and poly(monothioperoxydiphosphonamides) (S-O Bidentates, S-O Tridentates, S-O Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: monothioperoxydiphosphonamide, N-methylmonothioperoxydiphosphonamide, N-isopropylmonothioperoxydiphosphonamide, N-tert-butylmonothioperoxydiphosphonamide, N-phenylmonothioperoxydiphosphonamide, N-pentafluorophenylmonothioperoxydiphosphonamide, N-benzylmonothioperoxydiphosphonamide, N-cyclohexylmonothioperoxydiphosphonamide, N-norbornylmonothioperoxydiphosphonamide, N,N''-dimethylmonothioperoxydiphosphonamide, 20 N,N''-diisopropylmonothioperoxydiphosphonamide, N,N''-di-tert-butylmonothioperoxydiphosphonamide, N,N''-diphenylmonothioperoxydiphosphonamide, N,N''-di-pentafluorophenylmonothioperoxydiphosphonamide, N,N''-dibenzylmonothioperoxydiphosphonamide, N,N''-dicyclohexylmonothioperoxydiphosphonamide, and N,N''-dinorbornylmonothioperoxydiphosphonamide. [Note: the phosphite (P⁺³) valence of the

phosphorus atom makes stabilization of high valence metal ions much more difficult, though still possible.]

S-O Valence Stabilizer #16: Examples of monothioperoxydiphosphonic acids, bis(monothioperoxydiphosphonic acids), poly(monothioperoxydiphosphonic acids), and derivatives thereof (S-O Bidentates, S-O Tridentates, S-O Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: monothioperoxydiphosphonic acid, methylmonothioperoxydiphosphonic acid, isopropylmonothioperoxydiphosphonic acid, tert-butylmonothioperoxydiphosphonic acid, phenylmonothioperoxydiphosphonic acid, pentafluorophenylmonothioperoxydiphosphonic acid, benzylmonothioperoxydiphosphonic acid, cyclohexylmonothioperoxydiphosphonic acid, norbornylmonothioperoxydiphosphonic acid, dimethylmonothioperoxydiphosphonic acid, diisopropylmonothioperoxydiphosphonic acid, di-tert-butylmonothioperoxydiphosphonic acid, diphenylmonothioperoxydiphosphonic acid, di-pentafluorophenylmonothioperoxydiphosphonic acid, dibenzylmonothioperoxydiphosphonic acid, dicyclohexylmonothioperoxydiphosphonic acid, and dinorbornylmonothioperoxydiphosphonic acid. [Note: the phosphite (P⁺³) valence of the phosphorus atom makes stabilization of high valence metal ions much more difficult, though still possible.]

S-O Valence Stabilizer #17: Examples of monothiophosphoric acids (phosphorothioic acids), bis(monothiophosphoric acids), poly(monothiophosphoric acids), and derivatives thereof (S-O Bidentates, S-O Tridentates, S-O Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: monothiophosphoric acid, O-phenylmonothiophosphoric acid, O-benzylmonothiophosphoric acid, O-cyclohexylmonothiophosphoric acid, O-norbornylmonothiophosphoric acid, O,O-diphenylmonothiophosphoric acid, O,O-dibenzylmonothiophosphoric acid, O,O-dicyclohexylmonothiophosphoric acid, and O,O-dinorbornylmonothiophosphoric acid.

S-O Valence Stabilizer #18: Examples of phosphoro(dithioperoxoic) acids, bis[phosphoro(dithioperoxoic) acids], poly[phosphoro(dithioperoxoic) acids], and derivatives thereof (S-O Bidentates, S-O Tridentates, S-O Tetridentates) that meet the requirements for use

as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to:
phosphoro(dithioperoxoic) acid, O-phenylphosphoro(dithioperoxoic) acid, O-
benzylphosphoro(dithioperoxoic) acid, O-cyclohexylphosphoro(dithioperoxoic) acid, O-
norbornylphosphoro(dithioperoxoic) acid, O,O-diphenylphosphoro(dithioperoxoic) acid, O,O-
5 dibenzylphosphoro(dithioperoxoic) acid, O,O-dicyclohexylphosphoro(dithioperoxoic) acid, and
O,O-dinorbornylphosphoro(dithioperoxoic) acid.

S-O Valence Stabilizer #19: Examples of monothiophosphonic Acids (phosphonothioic acids),
bis(monothiophosphonic acids), poly(monothiophosphonic acids), and derivatives thereof (S-O

10 Bidentates, S-O Tridentates, S-O Tetridentates) that meet the requirements for use as “narrow
band” valence stabilizers for Ce⁺⁴ include, but are not limited to: monothiophosphonic acid, O-
phenylmonothiophosphonic acid, O-benzylmonothiophosphonic acid, O-
cyclohexylmonothiophosphonic acid, O-norbornylmonothiophosphonic acid, O,P-
diphenylmonothiophosphonic acid, O,P-dibenzylmonothiophosphonic acid, O,P-
15 dicyclohexylmonothiophosphonic acid, and O,P-dinorbornylmonothiophosphonic acid. [Note:
the phosphite (P⁺³) valence of the phosphorus atom makes stabilization of high valence metal
ions much more difficult, though still possible.]

S-O Valence Stabilizer #20: Examples of phosphono(dithioperoxoic) acids,

20 bis[phosphono(dithioperoxoic) acids], poly[phosphono(dithioperoxoic) acids], and derivatives
thereof (S-O Bidentates, S-O Tridentates, S-O Tetridentates) that meet the requirements for use
as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to:
phosphono(dithioperoxoic) acid, O-phenylphosphono(dithioperoxoic) acid, O-
benzylphosphono(dithioperoxoic) acid, O-cyclohexylphosphono(dithioperoxoic) acid, O-
25 norbornylphosphono(dithioperoxoic) acid, O,P-diphenylphosphono(dithioperoxoic) acid, O,P-
dibenzylphosphono(dithioperoxoic) acid, O,P-dicyclohexylphosphono(dithioperoxoic) acid, and
O,P-dinorbornylphosphono(dithioperoxoic) acid. [Note: the phosphite (P⁺³) valence of the
phosphorus atom makes stabilization of high valence metal ions much more difficult, though
still possible.]

S-O Valence Stabilizer #21: Examples of beta-hydroxythioketones, beta-hydroxythioaldehydes, bis(beta-hydroxythioketones), bis(beta-hydroxythioaldehydes), poly(beta-hydroxythioketones), and poly(beta-hydroxythioaldehydes) (S-O Bidentates, S-O Tridentates, S-O Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 4-hydroxypentan-2-thione; 1,3-diphenyl-3-hydroxypropanethioaldehyde; 1,3-dibenzyl-3-hydroxypropanethioaldehyde; 1,3-dicyclohexyl-3-hydroxypropanethioaldehyde; 1,3-dinorbornyl-3-hydroxypropanethioaldehyde; 1,3-di(2-thienyl)-3-hydroxypropanethioaldehyde; 1,3-di(2-furyl)-3-hydroxypropanethioaldehyde; o-hydroxythioacetophenone; and beta-hydroxythiobenzophenone.

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S-O Valence Stabilizer #22: Examples of beta-mercaptopketones, beta-mercptoaldehydes, bis(beta-mercaptopketones), bis(beta-mercptoaldehydes), poly(beta-mercaptopketones), and poly(beta-mercptoaldehydes) (S-O Bidentates, S-O Tridentates, S-O Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 4-mercaptopentan-2-one; 1,3-diphenyl-3-mercaptopropanal; 1,3-dibenzyl-3-mercaptopropanal; 1,3-dicyclohexyl-3-mercaptopropanal; 1,3-dinorbornyl-3-mercaptopropanal; 1,3-di(2-thienyl)-3-mercaptopropanal; 1,3-di(2-furyl)-3-mercaptopropanal; 3-mercpto-1,5-pentanodialdehyde; o-mercptoacetophenone; 5-mercpto-1,4-naphthoquinone; 1-mercptoacridone; 1-mercptoanthraquinone; 1,8-dimercptoanthraquinone; and beta-mercaptobenzophenone.

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S-O Valence Stabilizer #23: Examples of N-(aminomethylol)thioureas [N-(aminohydroxymethyl)thioureas], bis[N-(aminomethylol)thioureas], and poly[N-(aminomethylol)thioureas] (S-O Bidentates, S-O Tridentates, S-O Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: N’-(aminohydroxymethyl)thiourea; N,N”-dimethyl-N’-(aminohydroxymethyl)thiourea; N,N’-diethyl-N’-(aminohydroxymethyl)thiourea; N,N”-isopropyl-N’-(aminohydroxymethyl)thiourea; N,N”-diphenyl-N’-(aminohydroxymethyl)thiourea; N,N”-dibenzyl-N’-(aminohydroxymethyl)thiourea; N,N”-dicyclohexyl-N’-(aminohydroxymethyl)thiourea; and N,N”-dinorbornyl-N’-(aminohydroxymethyl)thiourea.

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S-O Valence Stabilizer #24: Examples of N-(aminomethylthiol)ureas [N-(aminomercaptomethyl)ureas], bis[N-(aminomethylthiol)ureas], and poly[N-(aminomethylthiol)ureas] (S-O Bidentates, S-O Tridentates, S-O Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to:

5 N’-(aminomercaptomethyl)urea; N,N”-dimethyl-N’-(aminomercaptomethyl)urea; N,N’-diethyl-N’-(aminomercaptomethyl)urea; N,N”-isopropyl-N’-(aminomercaptomethyl)urea; N,N”-diphenyl-N’-(aminomercaptomethyl)urea; N,N”-dibenzyl-N’-(aminomercaptomethyl)urea; N,N”-dicyclohexyl-N’-(aminomercaptomethyl)urea; and N,N”-dinorbornyl-N’-(aminomercaptomethyl)urea.

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S-O Valence Stabilizer #25: Examples of monothiooxamides, bis(monothiooxamides), and poly(monothiooxamides) (S-O Bidentates, S-O Tridentates, S-O Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: monothiooxamide, N-methylthiooxamide; N-ethylthiooxamide; N-isopropylthiooxamide; N-phenylthiooxamide; N-benzylthiooxamide; N-cyclohexylthiooxamide; N-norbornylthiooxamide; N,N’-dimethylthiooxamide; N,N’-diethylthiooxamide; N,N’-diisopropylthiooxamide; N,N’-diphenylthiooxamide; N,N’-dibenzylthiooxamide; N,N’-dicyclohexylthiooxamide; and N,N’-dinorbornylthiooxamide.

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S-O Valence Stabilizer #26: Examples of beta-mercpto carboxylic acids, bis(beta-mercpto carboxylic acids), poly(beta-mercpto carboxylic acids), and derivatives thereof (S-O Bidentates, S-O Tridentates, S-O Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: methyl 3-mercaptopropanoate; methyl 3-mercaptopbutanoate; ethyl 3-mercaptopbutanoate; phenyl 3-mercaptopbutanoate; cyclohexyl 3-mercaptopbutanoate; norbornyl 3-mercaptopbutanoate; methyl beta-mercaptophydrocinnamate; ethyl beta-mercaptophydrocinnamate; phenyl beta-mercaptophydrocinnamate; methyl o-mercaptopbenzoate; ethyl o-mercaptopbenzoate; phenyl o-mercaptopbenzoate; cyclohexyl o-mercaptopbenzoate; (2-benzothiazolylthio) succinic acid (mtbs); norbornyl o-mercaptopbenzoate; and 3-[(benzothiazol-2-yl)thio]propionic acid.

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S-O Valence Stabilizer #27: Examples of beta-mercaptop thiocarboxylic acids, bis(beta-mercaptop thiocarboxylic acids), poly(beta-mercaptop thiocarboxylic acids), and derivatives thereof (S-O Bidentates, S-O Tridentates, S-O Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: methyl 3-

5 mercaptothiobutanoate; ethyl 3-mercaptop thiobutanoate; phenyl 3-mercaptop thiobutanoate; cyclohexyl 3-mercaptop thiobutanoate; norbornyl 3-mercaptop thiobutanoate; methyl beta-mercaptop thiocinnamate; ethyl beta-mercaptop thiocinnamate; phenyl beta-mercaptop thiocinnamate; methyl o-mercaptop thiobenzoate; ethyl o-mercaptop thiobenzoate; phenyl o-mercaptop thiobenzoate; cyclohexyl o-mercaptop thiobenzoate; norbornyl o-mercaptop thiobenzoate; and (alkylthio)oxoethyl alkyl(aryl) disulfides.

S-O Valence Stabilizer #28: Examples of beta-hydroxy thiocarboxylic acids, bis(beta-hydroxy thiocarboxylic acids), poly(beta-hydroxy thiocarboxylic acids), and derivatives thereof (S-O Bidentates, S-O Tridentates, S-O Tetridentates) that meet the requirements for use as “narrow

15 band” valence stabilizers for Ce⁺⁴ include, but are not limited to: methyl 3-hydroxythiobutanoate; ethyl 3-hydroxythiobutanoate; phenyl 3-hydroxythiobutanoate; cyclohexyl 3-hydroxythiobutanoate; norbornyl 3-hydroxythiobutanoate; methyl beta-hydroxythiocinnamate; ethyl beta-hydroxythiocinnamate; phenyl beta-hydroxythiocinnamate; methyl o-hydroxythiobenzoate; ethyl o-hydroxythiobenzoate; phenyl o-hydroxythiobenzoate; cyclohexyl o-hydroxythiobenzoate; and norbornyl o-hydroxythiobenzoate.

S-O Valence Stabilizer #29: Examples of beta-mercaptop carboxamides, bis(beta-mercaptop carboxamides), poly(beta-mercaptop carboxamides), and derivatives thereof (S-O Bidentates, S-O Tridentates, S-O Tetridentates) that meet the requirements for use as “narrow band” valence

25 stabilizers for Ce⁺⁴ include, but are not limited to: N-methyl 3-mercaptop butanamide; N-ethyl 3-mercaptop butanamide; N-phenyl 3-mercaptop butanamide; N-cyclohexyl 3-mercaptop butanamide; N-norbornyl 3-mercaptop butanamide; N-methyl o-mercaptop benzamide; N-ethyl o-mercaptop benzamide; N-phenyl o-mercaptop benzamide; N-cyclohexyl o-mercaptop benzamide; and N-norbornyl o-mercaptop benzamide.

S-O Valence Stabilizer #30: Examples of S-alkylthiocarboxylic Acids, S-arylthiocarboxylic Acids, and S,S-thiobiscarboxylic Acids (S-O Bidentates and S-O Tridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: (methylthio)acetic acid; (methylthio)benzoic acid; (methylthio)nicotinic acid; (methylthio)naphthoic acid; (phenylthio)acetic acid; (phenylthio)benzoic acid; (phenylthio)naphthoic acid; (norbornylthio)acetic acid; (norbornylthio)benzoic acid; (norbornylthio)naphthoic acid; thiobisacetic acid; thiobisbenzoic acid; and thiobisnaphthoic acid.

S-O Valence Stabilizer #31: Examples of S-alkyldisulfidocarboxylic acids, S-aryldisulfidocarboxylic acids, and S,S'-disulfidobiscarboxylic acids (S-O Bidentates and S-O Tridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: (methyldisulfido)acetic acid; (methyldisulfido)benzoic acid; (methyldisulfido)nicotinic acid; (methyldisulfido)naphthoic acid; (phenyldisulfido)acetic acid; (phenyldisulfido)benzoic acid; (phenyldisulfido)naphthoic acid; (norbornyldisulfido)acetic acid; (norbornyldisulfido)benzoic acid; (norbornyldisulfido)naphthoic acid; S,S'-disulfidobisacetic acid; S,S'-disulfidobisbenzoic acid; and S,S'-disulfidobisnaphthoic acid.

S-O Valence Stabilizer #32: Examples of monothiomonocarboxylic acids, dithiodicarboxylic acids, bis(monothiomonocarboxylic acids), bis(dithiodicarboxylic acids), poly(monothiomonocarboxylic acids), poly(dithiodicarboxylic acids), and derivatives thereof (S-O Bidentates and S-O Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: thioacetic acid; thiopropionic acid; thiobenzoic acid; thiophenylacetic acid; thiocyclohexanoic acid; thiofuroic acid; thionaphthoic acid; phenyl thioacetate; phenyl thiopropionate; phenyl thiobenzoate; phenyl thiocyclohexanoate; phenyl thiofuroate; phenyl thionaphthoate; dithiooxalic acid (dto); monothiooxalic acid (mtox); dithiomalonic acid; dithiosuccinic acid; diphenyl dithiooxalate; diphenyl dithiomalonate; and diphenyl dithiosuccinate.

S-O Valence Stabilizer #33: Examples of monothiocarbonates and bis(monothiocarbonates) (S-O Bidentates and S-O Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: S,O-diethyldithiocarbonate; S,O-

diisopropyldithiocarbonate; S,O-diphenyldithiocarbonate; S,O-dibenzylidithiocarbonate; S,O-dicyclohexyldithiocarbonate; and S,O-dinorbornyldithiocarbonate.

S-O Valence Stabilizer #34: Examples of monothiocarbazates (monothiocarbazides),
5 bis(monothiocarbazates), and poly(monothiocarbazates) (S-O Bidentates, S-O Tridentates, and
S-O Tetridentates; or possibly N-S Bidentates, N-S Tridentates, and N-S Tetridentates) that
meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not
limited to: N,N'-dimethylmonothiocarbazate; N,N'-di(trifluoromethyl)monothiocarbazate; N,N'-
diethylmonothiocarbazate; N,N'-diphenylmonothiocarbazate; N,N'-dibenzylmonothiocarbazate;
10 N,N'-di(pentafluorophenyl)monothiocarbazate; N,N'-dicyclohexylmonothiocarbazate; and N,N'-
dinorbornylmonothiocarbazate.

S-O Valence Stabilizer #35: Examples of mercapto alcohols and silylmercaptoalcohols,
bis(mercaptop alcohols and silylmercaptoalcohols), and poly(mercaptop alcohols and
15 silylmercaptoalcohols) (S-O Bidentates, S-O Tridentates, S-O Tetridentates) that meet the
requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to:
2-mercptoethanol (mel); 3-mercaptopropanol (mpl); 2-mercaptophenol; 2-
mercaptocyclohexanol; 3-mercato-2-norneol; 2-mercaptopyridine 1-oxide; 1,4-thioxane;
thiodialkanols; 2-(trimethoxysilyl)-1-ethanethiol (tmset); 3-(trimethoxysilyl)-1-propanethiol
20 (tmspt); o-hydroxythiophenols; o-(O-hydroxyalkyl(aryl))thiophenols; and o-(S-
thioalkyl(aryl))phenols.

S-O Valence Stabilizer #36: Examples of monothiocarbimates, bis(monothiocarbimates), and
poly(monothiocarbimates) (S-O Bidentates, S-O Tridentates, and S-O Tetridentates) that meet
25 the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not
limited to: methylmonothiocarbimate; trifluoromethylmonothiocarbimate;
ethylmonothiocarbimate; propylmonothiocarbimate; isopropylmonothiocarbimate;
butylmonothiocarbimate; tertbutylmonothiocarbimate; cyanomonothiocarbimate;
cyanamidomonothiocarbimate; azidomonothiocarbimate; phenylmonothiocarbimate;
30 pentafluorophenylmonothiocarbimate; benzylmonothiocarbimate; naphthylmonothiocarbimate;

cyclohexylmonothiocarbimate; norbornylmonothiocarbimate; and adamantylmonothiocarbimate.
[Note: carbimates tend to stabilize lower oxidation states in metal ions.]

S-O Valence Stabilizer #37: Examples of alkyl- and aryl- monothioborates and
5 bis(monothioborates) (S-O Bidentates and S-O Tetridentates) that meet the requirements for use
as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: O,O'-diethyl
monothioborate; O,O'-diisopropyl monothioborate; O,O'-diphenyl monothioborate; O,O'-
dibenzyl monothioborate; O,O'-dicyclohexyl monothioborate; and O,O'-dinorbornyl
monothioborate.

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S-O Valence Stabilizer #38: Examples of alkyl- and aryl- monothioboronates and
bis(monothioboronates) (S-O Bidentates and S-O Tetridentates) that meet the requirements for
use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diethyl
monothioboronate; diisopropyl monothioboronate; diphenyl monothioboronate; dibenzyl
15 monothioboronate; dicyclohexyl monothioboronate; and dinorbornyl monothioboronate. [Note:
boronates tend to stabilize lower oxidation states in metal ions.]

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S-O Valence Stabilizer #39: Examples of monothioarsonic acids (arsonothioic acids),
bis(monothioarsonic acids), poly(monothioarsonic acids), and derivatives thereof (S-O
20 Bidentates, S-O Tridentates, S-O Tetridentates) that meet the requirements for use as “narrow
band” valence stabilizers for Ce⁺⁴ include, but are not limited to: monothioarsonic acid, O-
phenylmonothioarsonic acid, O-benzylmonothioarsonic acid, O-cyclohexylmonothioarsonic
acid, O-norbornylmonothioarsonic acid, O,O-diphenylmonothioarsonic acid, O,O-
25 dibenzylmonothioarsonic acid, O,O-dicyclohexylmonothioarsonic acid, and O,O-
dinorbornylmonothioarsonic acid.

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S-O Valence Stabilizer #40: Examples of heterocyclic rings containing one or two sulfur atoms
and having at least one additional oxygen atom binding site not in a ring (S-O Bidentates, S-O
Tridentates, S-O Tetridentates, or S-O Hexadentates) that meet the requirements for use as
30 “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-thiopheneethanol (2-
(2-thienyl)ethanol); 2-propionylthiophene (1-(2-thienyl)-1-propanone); N,N'-thiobisphthalimide;

1,1'-thiocarbonyldi-2-pyridone; 2-thiopheneacetic acid; 2-thiophenecarboxaldehyde; 2-thiophenecarboxamide; 2-thiophenecarboxylic acid; 2,5-thiophenedicarboxaldehyde; 2,5-thiophenedicarboxylic acid; 2-thiophenemethanol; 2-thiophenone; thiotetronic acid; alkyl(aryl) 5 2-thienyl ketones; dithienyl ketone; 1,3-dithiane-2-carboxylic acid; and 1,3-dithiolane-2-carboxylic acid.

S-O Valence Stabilizer #41: Examples of heterocyclic rings containing one or two oxygen atoms and having at least one additional sulfur atom binding site not in a ring (S-O Bidentates, S-O

Tridentates, S-O Tetridentates, or S-O Hexadentates) that meet the requirements for use as

10 “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-furanethanethiol (2-(2-furyl)ethanethiol); 1-(2-furyl)-1-propanethione); 2-furanthioacetic acid; 2-furanthiocarboxaldehyde; 2-furanthiocarboxamide; 2-furanthiocarboxylic acid; 2,5-furandithiocarboxaldehyde; 2,5-furandithiocarboxylic acid; 2-furanmethanethiol; 2-furanthione; furfuryl disulfide; furfuryl mercaptan; furfuryl sulfide; and furfuryl methyl disulfide.

15 S-O Valence Stabilizer #42: Examples of heterocyclic rings containing one or two sulfur atoms and having at least one additional oxygen atom binding site in a separate ring (S-O Bidentates, S-O Tridentates, S-O Tetridentates, or S-O Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-(2-furyl)thiophene; 2,5-(2-furyl)thiophene; 2-(2-furyl)thiopyran; and 2,5-(2-furyl)thiopyran.

20 S-O Valence Stabilizer #43: Examples of two-, three-, four-, five-, six-, seven-, eight-, nine-, and ten-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of sulfur

25 (usually thiol, mercapto, or thiocabonyl groups) or oxygen (hydroxy, carboxy, or carbonyl groups) and are not contained in component heterocyclic rings (S-O Bidentates, S-O Tridentates, S-O Tetridentates, and S-O Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: thiaoxacyclobutane ([4]aneOS); thiaoxacyclopentane ([5]aneOS); thiaoxacyclohexane ([6]aneOS); thiaoxacycloheptane ([7]aneOS); thiaoxacyclooctane ([8]aneOS); thiaoxacyclobutene ([4]eneOS); thiaoxacyclopentene ([5]eneOS); thiaoxacyclohexene ([6]eneOS); thiaoxacycloheptene

([7]eneOS); thiaoxacyclooctene ([8]eneOS); dithiaoxacyclohexane ([6]aneOS₂);
dithiaoxacycloheptane ([7]aneOS₂); dithiaoxacyclooctane ([8]aneOS₂); dithiaoxacyclononane
([9]aneOS₂); dithiaoxacyclodecane ([10]aneOS₂); dithiaoxacycloundecane ([11]aneOS₂);
dithiaoxacyclododecane ([12]aneOS₂); dithiaoxacyclohexene ([6]eneOS₂);
5 dithiaoxacycloheptene ([7]eneOS₂); dithiaoxacyclooctene ([8]eneOS₂); dithiaoxacyclononene
([9]eneOS₂); dithiaoxacyclodecene ([10]eneOS₂); dithiaoxacycloundecene ([11]eneOS₂);
dithiaoxacyclododecene ([12]eneOS₂); dithiadioxacyclooctane ([8]aneO₂S₂);
dithiadioxacyclononane ([9]aneO₂S₂); dithiadioxacyclodecene ([10]aneO₂S₂);
dithiadioxacycloundecane ([11]aneO₂S₂); dithiadioxacyclododecene ([12]aneO₂S₂);
10 dithiadioxacyclotridecane ([13]aneO₂S₂); dithiadioxacyclotetradecane ([14]aneO₂S₂);
dithiadioxacyclopentadecane ([15]aneO₂S₂); dithiadioxacyclohexadecane ([16]aneO₂S₂);
dithiadioxacycloheptadecane ([17]aneO₂S₂); dithiadioxacyclooctadecane ([18]aneO₂S₂);
dithiadioxacyclononadecane ([19]aneO₂S₂); dithiadioxacycloicosane ([20]aneO₂S₂);
dithiadioxacyclooctadiene ([8]dieneO₂S₂); dithiadioxacyclononadiene ([9]dieneO₂S₂);
15 dithiadioxacyclodecadiene ([10]dieneO₂S₂); dithiadioxacycloundecadiene ([11]dieneO₂S₂);
dithiadioxacyclododecadiene ([12]dieneO₂S₂); dithiadioxacyclotridecadiene ([13]dieneO₂S₂);
dithiadioxacyclotetradecadiene ([14]dieneO₂S₂); dithiadioxacyclopentadecadiene
([15]dieneO₂S₂); dithiadioxacyclohexadecadiene ([16]dieneO₂S₂);
dithiadioxacycloheptadecadiene ([17]dieneO₂S₂); dithiadioxacyclooctadecadiene
([18]dieneO₂S₂); dithiadioxacyclononadecadiene ([19]dieneO₂S₂); and
20 dithiadioxacycloicosadiene ([20]dieneO₂S₂).

S-O Valence Stabilizer #44: Examples of four-, five-, six-, seven-, eight-, nine-, or ten-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of sulfur or oxygen and are contained in component heterocyclic rings (S-O Tridentates, S-O Tetradentates, or S-O Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: difuranthiophenes; difurantrithiophenes; trifurantrithiophenes; and tetrafurantrathiophenes.

S-O Valence Stabilizer #45: Examples of four-, five-, six-, seven-, eight-, nine-, or ten-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of sulfur or oxygen and are contained in a combination of heterocyclic rings and thiol, mercapto, thiocarbonyl, hydroxy, carboxy, and carbonyl groups (S-O Tridentates, S-O Tetridentates, or S-O Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dithiadifurandithiophenes; tetrathiadifurandithiophenes; trithia trifurantrithiophenes; trithia trifurantrithiophenes; tetrathiatetrafuran tetra thiophenes; and octathiatetrafuran tetra thiophenes.

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S-O Valence Stabilizer #46: Examples of sulfoxides that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dimethylsulfoxide (DMSO); diethylsulfoxide; diphenylsulfoxide; and tetrahydrothiophene oxide.

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S-O Valence Stabilizer #47: Examples of sulfones that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dimethyl sulfone; diethyl sulfone; and diphenyl sulfone.

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S-O Valence Stabilizer #48: Examples of sulfur dioxide ligands that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: sulfur dioxide (-SO₂) ligands. [Note: sulfur dioxide is a reducing agent, and complexed metal ions therefore tend to prefer lower oxidation states.]

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N-P Valence Stabilizer #1: Examples of aminoaryl phosphines and iminoaryl phosphines (N-P Bidentates, N-P Tridentates, and N-P Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: tri(2-aminophenyl)phosphine; tri(2-aminophenyl)phosphine oxide; and tri(2-aminophenyl)phosphine sulfide.

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N-P Valence Stabilizer #2: Examples of heterocyclic rings containing one, two, three, or four nitrogen atoms and having at least one additional phosphorus atom binding site not in a ring (N-P

Bidentates, N-P Tridentates, N-P Tetridentates, or N-P Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: tri(2-imidazolyl)phosphine; tri(2-pyrrolyl)phosphine; tri(2-pyridyl)phosphine; tri(2-imidazolyl)phosphine oxide; tri(2-pyrrolyl)phosphine oxide; tri(2-pyridyl)phosphine oxide; tri(2-imidazolyl)phosphine sulfide; tri(2-pyrrolyl)phosphine sulfide; and tri(2-pyridyl)phosphine sulfide.

N-P Valence Stabilizer #3: Examples of heterocyclic rings containing one, two, or three phosphorus atoms and having at least one additional nitrogen atom binding site not in a ring (N-P Bidentates, N-P Tridentates, N-P Tetridentates, or N-P Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-aminophosphole; 2,5-diaminophosphole; 2-(aminomethyl)phosphole; 2,5-di(aminomethyl)phosphole; 2-aminophosphorin; 2,6-diaminophosphorin; 2-(aminomethyl)phosphorin; 2,6-di(aminomethyl)phosphorin; triaminocyclotriphosphazenes; and hexaminocyclotriphosphazenes.

N-P Valence Stabilizer #4: Examples of heterocyclic rings containing one, two, three, or four nitrogen atoms and having at least one additional phosphorus atom binding site in a separate ring (N-P Bidentates, N-P Tridentates, N-P Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-(2-pyrrolyl)phosphole; 2,5-di(2-pyrrolyl)phosphole; 2-(2-pyridyl)phosphorin; and 2,6-(2-pyridyl)phosphorin.

N-P Valence Stabilizer #5: Examples of two-, three-, four-, five-, six-, seven-, eight-, nine-, and ten-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of nitrogen (usually amine or imine groups) or phosphorus and are not contained in component heterocyclic rings (N-P Bidentates, N-P Tridentates, N-P Tetridentates, and N-P Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: cyclobiphosphazenes; cyclotriphosphazenes; cyclotetraphosphazenes; cyclopentaphosphazenes;

cyclohexaphosphazenes; diphosphatetraazacyclooctatetraenes; diphospho-s-triazines; and phospho-s-triazines.

N-P Valence Stabilizer #6: Examples of four-, five-, six-, seven-, eight-, nine-, or ten-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of nitrogen or phosphorus and are contained in component heterocyclic rings (N-P Bidentates, N-P Tridentates, N-P Tetridentates, or N-P Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diphospholedipyrroles; 10 diphosphorindipyridines; triphospholetripyrrroles; triphosphorintripyridines; tetraphospholetetrapyrrroles; and tetraphosphorintetrapyridines.

N-P Valence Stabilizer #7: Examples of four-, five-, six-, seven-, eight-, nine-, or ten-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of nitrogen or phosphorus and are contained in a combination of heterocyclic rings and amine, imine, and phosphine groups (N-P Bidentates, N-P Tridentates, N-P Tetridentates, or N-P Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: azaphosphatetraphyrins; diazadiphosphatetraphyrins; azaphosphahexaphyrins; 20 diazadiphosphahexaphyrins; triazatriphosphahexaphyrins; and apholate.

S-P Valence Stabilizer #1: Examples of thioaryl phosphines (S-P Bidentates, S-P Tridentates, S-P Tetridentates, and S-P Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: tri(2-mercaptophenyl)phosphine; tri(2-mercaptophenyl)phosphine oxide; and tri(2-mercaptophenyl)phosphine sulfide.

S-P Valence Stabilizer #2: Examples of heterocyclic rings containing one or two sulfur atoms and having at least one additional phosphorus atom binding site not in a ring (S-P Bidentates, S-P Tridentates, S-P Tetridentates, or S-P Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: tri(2-thiophene)phosphine; tri(2-thiopyran)phosphine; tri(2-thiophene)phosphine oxide; tri(2-

thiopyran)phosphine oxide; tri(2-thiophene)phosphine sulfide; and tri(2-thiopyran)phosphine sulfide.

S-P Valence Stabilizer #3: Examples of heterocyclic rings containing one, two, or three phosphorus atoms and having at least one additional sulfur atom binding site not in a ring (S-P Bidentates, S-P Tridentates, S-P Tetridentates, or S-P Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-mercaptophosphole; 2,5-dimercaptophosphole; 2-(mercaptopethyl)phosphole; 2,5-di(mercaptopethyl)phosphole; 2-mercaptophosphorin; 2,6-dimercaptophosphorin; 2-(mercaptopethyl)phosphorin; and 2,6-di(mercaptopethyl)phosphorin.

S-P Valence Stabilizer #4: Examples of heterocyclic rings containing one or two sulfur atoms and having at least one additional phosphorus atom binding site in a separate ring (S-P Bidentates, S-P Tridentates, S-P Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-(2-thienyl)phosphole; 2,5-di(2-thienyl)phosphole; 2-(2-thienyl)phosphorin; and 2,6-(2-thienyl)phosphorin.

S-P Valence Stabilizer #5: Examples of two-, three-, four-, five-, six-, seven-, eight-, nine-, and ten-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of sulfur (usually thiol, mercapto, or thiocarbonyl groups) or phosphorus and are not contained in component heterocyclic rings (S-P Bidentates, S-P Tridentates, S-P Tetridentates, and S-P Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: phosphathiacyclobutane ([4]anePS); phosphathiacyclopentane ([5]anePS); phosphathiacyclohexane ([6]anePS); phosphathiacycloheptane ([7]anePS); phosphathiacyclooctane ([8]anePS); diphosphathiacyclohexane ([6]aneSP₂); diphosphathiacycloheptane ([7]aneSP₂); diphosphathiacyclooctane ([8]aneSP₂); diphosphathiacyclononane ([9]aneSP₂); diphosphathiacyclodecane ([10]aneSP₂); diphosphathiacycloundecane ([11]aneSP₂); diphosphathiacyclododecane ([12]aneSP₂); diphosphadithiacyclooctane ([8]aneS₂P₂); diphosphadithiacyclononane ([9]aneS₂P₂); diphosphadithiacyclodecane ([10]aneS₂P₂); diphosphadithiacycloundecane ([11]aneS₂P₂);

diphosphadithiacyclododecane ([12]aneS₂P₂); diphosphadithiacyclotridecane ([13]aneS₂P₂);
diphosphadithiacyclotetradecane ([14]aneS₂P₂); diphosphadithiacyclopentadecane ([15]aneS₂P₂);
diphosphadithiacyclohexadecane ([16]aneS₂P₂); diphosphadithiacycloheptadecane
([17]aneS₂P₂); diphosphadithiacyclooctadecane ([18]aneS₂P₂); diphosphadithiacyclononadecane
([19]aneS₂P₂); diphosphadithiacycloicosane ([20]aneS₂P₂).
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S-P Valence Stabilizer #6: Examples of four-, five-, six-, seven-, eight-, nine-, or ten-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of sulfur or phosphorus and are contained in component heterocyclic rings (S-P Bidentates, S-P Tridentates, S-P Tetradentates, or S-P Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diphospholedithiophenes; diphosphorindithiopyrans; triphospholetrithiophenes; triphosphorintrithiopyrans; tetraphospholetetrathiophenes; and tetraphosphorintetrathiopyrans.
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S-P Valence Stabilizer #7: Examples of four-, five-, six-, seven-, eight-, nine-, or ten-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of sulfur or phosphorus and are contained in a combination of heterocyclic rings and thiol, mercapto, thiocarbonyl, and phosphine groups (S-P Bidentates, S-P Tridentates, S-P Tetradentates, or S-P Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: thiaphospatetraphyrins; dithiadiphospatetraphyrins; thiaphosphahexaphyrins; dithiadiphosphahexaphyrins; and trithiatriphosphahexaphyrins.
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P-O Valence Stabilizer #1: Examples of hydroxyaryl phosphines (P-O Bidentates, P-O Tridentates, P-O Tetradentates, and P-O Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: tri(2-hydroxyphenyl)phosphine; tri(2-hydroxyphenyl)phosphine oxide; and tri(2-hydroxyphenyl)phosphine sulfide.
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P-O Valence Stabilizer #2: Examples of heterocyclic rings containing one or two oxygen atoms and having at least one additional phosphorus atom binding site not in a ring (P-O Bidentates, P-O Tridentates, P-O Tetridentates, or P-O Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: tri(2-furan)phosphine; tri(2-pyran)phosphine; tri(2-furan)phosphine oxide; tri(2-pyran)phosphine oxide; tri(2-furan)phosphine sulfide; and tri(2-pyran)phosphine sulfide.

P-O Valence Stabilizer #3: Examples of heterocyclic rings containing one, two, or three phosphorus atoms and having at least one additional oxygen atom binding site not in a ring (P-O Bidentates, P-O Tridentates, P-O Tetridentates, or P-O Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-hydroxyphosphole; 2,5-dihydroxyphosphole; 2-(hydroxymethyl)phosphole; 2,5-di(hydroxymethyl)phosphole; 2-hydroxyphosphorin; 2,6-dihydroxyphosphorin; 2-(hydroxymethyl)phosphorin; and 2,6-di(hydroxymethyl)phosphorin.

P-O Valence Stabilizer #4: Examples of heterocyclic rings containing one or two oxygen atoms and having at least one additional phosphorus atom binding site in a separate ring (P-O Bidentates, P-O Tridentates, P-O Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-(2-furyl)phosphole; 2,5-di(2-furyl)phosphole; 2-(2-furyl)phosphorin; and 2,6-(2-furyl)phosphorin.

P-O Valence Stabilizer #5: Examples of two-, three-, four-, five-, six-, seven-, eight-, nine-, and ten-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of oxygen (usually hydroxy, carboxy, or carbonyl groups) or phosphorus and are not contained in component heterocyclic rings (P-O Bidentates, P-O Tridentates, P-O Tetridentates, and P-O Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: phosphaoxacyclobutane ([4]anePO); phosphaoxacyclopentane ([5]anePO); phosphaoxacyclohexane ([6]anePO); phosphaoxacycloheptane ([7]anePO); phosphaoxacyclooctane ([8]anePO); diphosphaoxacyclohexane ([6]aneOP₂); diphosphaoxacycloheptane ([7]aneOP₂); diphosphaoxacyclooctane ([8]aneOP₂);

diphosphaoxacyclononane ([9]aneOP₂); diphosphaoxacyclodecane ([10]aneOP₂);
diphosphaoxacycloundecane ([11]aneOP₂); diphosphaoxacyclododecane ([12]aneOP₂);
diphosphadioxacyclooctane ([8]aneO₂P₂); diphosphadioxacyclononane ([9]aneO₂P₂);
diphosphadioxacyclodecane ([10]aneO₂P₂); diphosphadioxacycloundecane ([11]aneO₂P₂);
5 diphosphadioxacyclododecane ([12]aneO₂P₂); diphosphadioxacyclotridecane ([13]aneO₂P₂);
diphosphadioxacyclotetradecane ([14]aneO₂P₂); diphosphadioxacyclopentadecane
([15]aneO₂P₂); diphosphadioxacyclohexadecane ([16]aneO₂P₂);
diphosphadioxacycloheptadecane ([17]aneO₂P₂); diphosphadioxacyclooctadecane
([18]aneO₂P₂); diphosphadioxacyclononadecane ([19]aneO₂P₂); diphosphadioxacycloicosane
([20]aneO₂P₂); and dioxaphospholane.

P-O Valence Stabilizer #6: Examples of four-, five-, six-, seven-, eight-, nine-, or ten-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of oxygen or phosphorus
15 and are contained in component heterocyclic rings (P-O Bidentates, P-O Tridentates, P-O Tetridentates, or P-O Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diphospholedifurans; diphosphorindipyrans; triphospholetrifurans; triphosphorintripyrans; tetraphospholetetrafurans; and tetraphosphorintetrapyrans.

P-O Valence Stabilizer #7: Examples of four-, five-, six-, seven-, eight-, nine-, or ten-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of oxygen or phosphorus and are contained in a combination of heterocyclic rings and hydroxy, carboxy, carbonyl, and phosphine groups (P-O Bidentates, P-O Tridentates, P-O Tetridentates, or P-O Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: oxaphospatetraphyrins; dioxadiphospatetraphyrins; oxaphosphahexaphyrins; dioxadiphosphahexaphyrins; and trioxatriphosphahexaphyrins.

As Valence Stabilizer #1: Examples of monoarsines (As Monodentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to:

arsine, triphenylarsine, ticyclohexylarsine, methyldiphenylarsine, ethyldiphenylarsine, arsinonorbornane, and arsinoadamantane.

As Valence Stabilizer #2: Examples of diarsines (As Monodentates or As-As Bidentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: bis(diphenylarsino)methane, bis(diphenylarsino)ethane, bis(diphenylarsino)propane, bis(diphenylarsino)butane, bis(diphenylarsino)pentane, 1,2-diarsinobenzene, cyclohexane-1,2-diarsine, 1,2-bis(phenylbutylarsino)ethane, o-phenylenebis(methylphenylarsine) and o-phenylenebis(dimethylarsine) (diars). [Note: the aryl derivatives are air-stable, whereas the alkyl derivatives are air-sensitive and therefore unsuitable for these applications.]

As Valence Stabilizer #3: Examples of triarsines (As-As Bidentates, or As-As Tridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 1,1,5,9,9-pentaphenyl-1,5,9-triarsanonane, 3-methyl-3-(As,As-dimethyl)arsinomethyl-1,1,5,5-tetraphenyl-1,5-diarsapentane, As,As-[o-(As-dimethyl)arsinodiphenyl]-(As-phenyl)arsine, As,As-[o-(As-diphenyl)arsinodiphenyl]-(As-phenyl)arsine, hexahydro-2,4,6-trimethyl-1,3,5-triarsinazine. [Note: the aryl derivatives are air-stable, whereas the alkyl derivatives are air-sensitive and therefore unsuitable for these applications.]

As Valence Stabilizer #4: Examples of tetraarsines (As-As Bidentates, As-As Tridentates, or As-As Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 3,3-(As-diphenyl)arsinomethyl-1,1,5,5-tetraphenyl-1,5-diarsapentane. [Note: the aryl derivatives are air-stable, whereas the alkyl derivatives are air-sensitive and therefore unsuitable for these applications.]

As Valence Stabilizer #5: Examples of pentaarsines (As-As Bidentates, As-As Tridentates, or As-As Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 4-[2-(As-diphenyl)arsinoethyl]-1,1,7,10,10-pentaphenyl-1,4,7,10-tetraarsadecane. [Note: The aryl derivatives are air-stable, whereas the alkyl derivatives are air-sensitive and therefore unsuitable for these applications.]

As Valence Stabilizer #6: Examples of hexaarsines (As-As Bidentates, As-As Tridentates, As-As Tetridentates, or As-As Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: o-phenylenebis[di-3-(As-diphenyl)arsinopropylarsine]. [Note: the aryl derivatives are air-stable, whereas the alkyl derivatives are air-sensitive and therefore unsuitable for these applications.]

5 As Valence Stabilizer #7: Examples of 5-membered heterocyclic rings containing one arsenic atom (As Monodentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: arsole, azarsole, diazarsole, benzarsole, benzazarsole, 10 dibenzarsole, naphtharsole, naphthazarsole.

15 As Valence Stabilizer #8: Examples of 6-membered heterocyclic rings containing one arsenic atom (As Monodentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: arsenin, azarsenin, diazarsenin, benzarsenin, benzazarsenin, dibenzarsenin, naphtharsenin, and naphthazarstenin.

20 As Valence Stabilizer #9: Examples of 5-membered heterocyclic rings containing one arsenic atom and having at least one additional arsenic atom binding site not contained in a ring (As Monodentates, As-As Bidentates, As-As Tridentates, As-As Tetridentates, or As-As Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-(As-phenylarsino)arsole; 2,5-(As-phenylarsino)arsole; 2-(As-phenylarsino)benzarsole; 7-(As-phenylarsino)benzarsole; and 1,8-(As-phenylarsino)dibenzarsole.

25 As Valence Stabilizer #10: Examples of 6-membered heterocyclic rings containing one arsenic atom and having at least one additional arsenic atom binding site not contained in a ring (As Monodentates, As-As Bidentates, As-As Tridentates, As-As Tetridentates, or As-As Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2-(As-phenylarsino)arsenin; 2,5-(As-phenylarsino)arsenin; 2-(As-phenylarsino)benzarsenin; 7-(As-phenylarsino)benzarsenin; and 1,9-(As-phenylarsino)dibenzarsenin.

As Valence Stabilizer #11: Examples of 5-membered heterocyclic rings containing one arsenic atom and having at least one additional arsenic atom binding site contained in a ring (As Monodentates, As-As Bidentates, As-As Tridentates, As-As Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to:
5 2,2'-biarsole; 2,2',2"-triarsole; and 2,2'-bibenzarsole.

As Valence Stabilizer #12: Examples of 6-membered heterocyclic rings containing one arsenic atom and having at least one additional arsenic atom binding site contained in a ring (As Monodentates, As-As Bidentates, As-As Tridentates, As-As Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to:
10 2,2'-biarsenin; 2,2',2"-triarsenin; 2,2',2",2""-tetraarsenin; 2,2'-bibenzarsenin; and 8,8'-bibenzarsenin.

As Valence Stabilizer #13a: Examples of two-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein both binding sites are composed of arsenic and are not contained in component heterocyclic rings (As-As Bidentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: As,As-diphenyldiarsacyclobutane ([4]aneAs₂); As,As-diphenyldiarsacyclopentane ([5]aneAs₂); As,As-diphenyldiarsacyclohexane ([6]aneAs₂); As,As-diphenyldiarsacycloheptane ([7]aneAs₂); As,As-diphenyldiarsacyclooctane ([8]aneAs₂); As,As-diphenyldiarsacyclobutene ([4]eneAs₂); As,As-diphenyldiarsacyclopentene ([5]eneAs₂); As,As-diphenyldiarsacyclohexene ([6]eneAs₂); As,As-diphenyldiarsacycloheptene ([7]eneAs₂); and As,As-diphenyldiarsacyclooctene ([8]eneAs₂).
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As Valence Stabilizer #13b: Examples of three-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of arsenic and are not contained in component heterocyclic rings (As-As Tridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: As,As,As-triphenyltriarsacyclohexane ([6]aneAs₃); As,As,As-triphenyltriarsacycloheptane ([7]aneAs₃); As,As,As-triphenyltriarsacyclooctane ([8]aneAs₃); As,As,As-triphenyltriarsacyclononane ([9]aneAs₃); As,As,As-triphenyltriarsacyclodecane
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([10]aneAs₃); As,As,As-triphenyltriarsacycloundecane ([11]aneAs₃); As,As,As-triphenyltriarsacyclododecane ([12]aneAs₃); As,As,As-triphenyltriarsacyclohexatriene ([6]trieneAs₃); As,As,As-triphenyltriarsacycloheptatriene ([7]trieneAs₃); As,As,As-triphenyltriarsacyclooctatriene ([8]trieneAs₃); As,As,As-triphenyltriarsacyclononatriene ([9]trieneAs₃); As,As,As-triphenyltriarsacyclodecatriene ([10]trieneAs₃); As,As,As-triphenyltriarsacycloundecatriene ([11]trieneAs₃); and As,As,As-triphenyltriarsacyclododecatriene ([12]trieneAs₃).

As Valence Stabilizer #13c: Examples of four-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of arsenic and are not contained in component heterocyclic rings (As-As Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: As,As,As,As-tetraphenyltetraarsacyclooctane ([8]aneAs₄); As,As,As,As-tetraphenyltetraarsacyclononane ([9]aneAs₄); As,As,As,As-tetraphenyltetraarsacyclodecane ([10]aneAs₄); As,As,As,As-tetraphenyltetraarsacycloundecane ([11]aneAs₄); As,As,As,As-tetraphenyltetraarsacyclododecane ([12]aneAs₄); As,As,As,As-tetraphenyltetraarsacyclotridecane ([13]aneAs₄); As,As,As,As-tetraphenyltetraarsacyclotradecane ([14]aneAs₄); As,As,As,As-tetraphenyltetraarsacyclopentadecane ([15]aneAs₄); As,As,As,As-tetraphenyltetraarsacyclohexadecane ([16]aneAs₄); As,As,As,As-tetraphenyltetraarsacycloheptadecane ([17]aneAs₄); As,As,As,As-tetraphenyltetraarsacyclooctadecane ([18]aneAs₄); As,As,As,As-tetraphenyltetraarsacyclononadecane ([19]aneAs₄); and As,As,As,As-tetraphenyltetraarsacycloicosane ([20]aneAs₄).

As Valence Stabilizer #13d: Examples of six-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of arsenic and are not contained in component heterocyclic rings (As-As Tridentates, As-As Tetridentates, or As-As Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: As,As,As,As,As,As-hexaphenylhexaarsacyclododecane ([12]aneAs₆); As-As,As,As,As,As-

hexaphenylhexaarsacyclotridecane ([13]aneAs₆); As,As,As,As,As,As-
hexaphenylhexaarsacyclotetradecane ([14]aneAs₆); As,As,As,As,As,As-
hexaphenylhexaarsacyclopentadecane ([15]aneAs₆); As,As,As,As,As,As-
hexaphenylhexaarsacyclohexadecane ([16]aneAs₆); As,As,As,As,As,As-
5 hexaphenylhexaarsacycloheptadecane ([17]aneAs₆); As,As,As,As,As,As-
hexaphenylhexaarsacyclooctadecane ([18]aneAs₆); As,As,As,As,As,As-
hexaphenylhexaarsacyclononadecane ([19]aneAs₆); As,As,As,As,As,As-
hexaphenylhexaarsacycloicosane ([20]aneAs₆); As,As,As,As,As,As-
hexaphenylhexaarsacycloheneicosane ([21]aneAs₆); As,As,As,As,As,As-
10 hexaphenylhexaarsacyclodocosane ([22]aneAs₆); As,As,As,As,As,As-
hexaphenylhexaarsacyclotricosane ([23]aneAs₆); and As,As,As,As,As,As-
hexaphenylhexaarsacyclotetracosane ([24]aneAs₆).

15 As Valence Stabilizer #14a: Examples of four-membered macrocyclics, macrobicyclics, and
macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all
four binding sites are composed of arsenic and are contained in component 5-membered
heterocyclic rings (As-As Tetridentates) that meet the requirements for use as “narrow band”
valence stabilizers for Ce⁺⁴ include, but are not limited to: tetraarsoles.

20 As Valence Stabilizer #14b: Examples of six-membered macrocyclics, macrobicyclics, and
macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all
six binding sites are composed of arsenic and are contained in component 5-membered
heterocyclic rings (As-As Tetridentates and As-As Hexadentates) that meet the requirements for
use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: hexaarsoles.

25 As Valence Stabilizer #15a: Examples of four-membered macrocyclics, macrobicyclics, and
macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all
four binding sites are composed of arsenic and are contained in a combination of 5-membered
heterocyclic rings and arsine groups (As-As Tridentates, As-As Tetridentates) that meet the
30 requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to:
diarsatetraarsoles; and tetraarsatetraarsoles.

As Valence Stabilizer #15b: Examples of six-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all six binding sites are composed of arsenic and are contained in a combination of 5-membered heterocyclic rings and phosphine groups (As-As Tridentates, As-As Tetridentates, and As-As Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diarsahexaarsoles; and triarsahexaarsoles.

As Valence Stabilizer #16a: Examples of four-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all four binding sites are composed of arsenic and are contained in component 6-membered heterocyclic rings (As-As Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: cyclotetraarsenins.

As Valence Stabilizer #16b: Examples of six-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all six binding sites are composed of arsenic and are contained in component 6-membered heterocyclic rings (As-As Tridentates, As-As Tetridentates, and As-As Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: cyclohexaarsenins.

As Valence Stabilizer #17a: Examples of four-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all four binding sites are composed of arsenic and are contained in a combination of 6-membered heterocyclic rings and arsine groups (As-As Tridentates, As-As Tetridentates, or As-As Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diarsacyclotetraarsenins; and tetraarsacyclotetraarsenins.

As Valence Stabilizer #17b: Examples of six-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all six binding sites are composed of arsenic and are contained in a combination of 6-membered heterocyclic rings and arsine groups (As-As Tridentates, As-As Tetridentates, or As-As

Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diarsacyclohexaarsenins; and triarsacyclohexaarsenins.

Se Valence Stabilizer #1: Examples of monoselenoethers (Se Monodentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: hydrogen selenide, dimethyl selenide, diethyl selenide, dioctyl selenide, diphenyl selenide, dicyclohexyl selenide, tetramethylene selenide, trimethylene selenide, dimethylene selenide, and selenobicycloheptane.

Se Valence Stabilizer #2: Examples of diselenoethers (Se Bidentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2,5-dimethyl-3,6-diselenaoctane; 2,5-diselenahexane; 2,6-diselenahheptane; 3,7-diselenanonane; 3,6-diselenaoctane; 3-but enyl butyl selenoether (bbs); 4-pentenyl butyl selenoether (pbs); 3-but enyl phenyl selenoether (bps); and 4-pentenyl phenyl selenoether (pps).

Se Valence Stabilizer #3: Examples of triselenoethers (Se Bidentates or Se Tridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 1,3,5-triselenane; 2,5,8-triselenanonane; 3,6,9-triselenaundercane; and 2,6,10-triselenaundercane.

Se Valence Stabilizer #4: Examples of tetraselenoethers (Se Bidentates, Se Tridentates, or Se Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2,6,10,14-tetraselenapentadecane and 2,5,8,11-tetraselenadodecane.

Se Valence Stabilizer #5a: Examples of 5-membered heterocyclic rings containing one selenium atom (Se Monodentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dihydroselenophene, selenophene, selenazole, selenapyrrolidine, selenaphospholene, selenaphosphole, oxaselenole, selenadiazole, selenatriazole, benzodihydroselenophene, benzoselenophene, benzoselenazole, benzoselenaphosphole, dibenzoselenophene, and naphthoselenophene.

Se Valence Stabilizer #5b: Examples of 5-membered heterocyclic rings containing two selenium atoms (Se Monodentates or Se Bidentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diselenole, benzodiselenole, and naphthodiselenole.

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Se Valence Stabilizer #6a: Examples of 6-membered heterocyclic rings containing one selenium atom (Se Monodentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dihydroselenopyran, selenopyran, selenazine, selenadiazine, selenaphosphorin, selenadiphosphorin, oxaselenin, benzoselenopyran, dibenzoselenopyran, and naphthoselenopyran.

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Se Valence Stabilizer #6b: Examples of 6-membered heterocyclic rings containing two selenium atoms (Se Monodentates or Se Bidentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dihydroselenin, diselenin, benzodiselenin, dibenzodiselenin, and naphthodiselenin.

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Se Valence Stabilizer #7: Examples of 5-membered heterocyclic rings containing one selenium atom and having at least one additional selenium atom binding site not contained in a ring (Se Monodentates, Se-Se Bidentates, Se-Se Tridentates, Se-Se Tetridentates, or Se-Se Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2,5-diseleno-2,5-dihydroselenophene; 2,5-bis(selenomethyl)-2,5-dihydroselenophene; 2,5-bis(2-selenophenyl)-2,5-dihydroselenophene; 2,5-diseleno(selenophene); 2,5-bis(selenomethyl)selenophene; 2,5-bis(2-selenophenyl)selenophene; 2,5-diseleno(selenazole); 2,5-bis(selenomethyl)selenazole; 2,5-bis(2-selenophenyl)selenazole; and 2,5-diseleno-1,3,4-selenadiazole [bismuthselenol].

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Se Valence Stabilizer #8: Examples of 6-membered heterocyclic rings containing one selenium atom and having at least one additional selenium atom binding site not contained in a ring (Se Monodentates, Se-Se Bidentates, Se-Se Tridentates, Se-Se Tetridentates, or Se-Se Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 2,6-diseleno-2,5-dihydroselenopyran; 2,6-bis(selenomethyl)-2,5-

dihydroselenopyran; 2,6-bis(2-selenophenyl)-2,5-dihydroselenopyran; 2,6-diseleno(selenopyran); 2,6-bis(selenomethyl)selenopyran; 2,6-bis(2-selenophenyl)selenopyran; 2,6-diseleno(selenazine); 2,6-bis(selenomethyl)selenazine; 2,6-bis(2-selenophenyl)selenazine; 2,6-diseleno-1,3,5-selenadiazine; 2-seleno-1-benzoselenopyran; 8-seleno-1-benzoselenopyran; 5 and 1,9-diselenodibenzoselenopyran.

Se Valence Stabilizer #9: Examples of 5-membered heterocyclic rings containing one selenium atom and having at least one additional selenium atom binding site contained in a ring (Se Monodentates, Se-Se Bidentates, Se-Se Tridentates, Se-Se Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 10 2,2'-bi-2,5-dihydroselenophene; 2,2',2"-tri-2,5-dihydroselenophene; 2,2'-biselenophene; 2,2',2"-triselenophene; 2,2'-biselenazole; 5,5'-biselenazole; 2,2'-bi-1,3,4-selenadiazole; 2,2'-biselenanaphthene; 2,2'-bibenzoselenazole; and 1,1'-bis(dibenzoselenophene).

15 Se Valence Stabilizer #10: Examples of 6-membered heterocyclic rings containing one selenium atom and having at least one additional selenium atom binding site contained in a ring (Se Monodentates, Se-Se Bidentates, Se-Se Tridentates, Se-Se Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 20 2,2'-bi-2,5-dihydroselenopyran; 2,2',2"-tri-2,5-dihydroselenopyran; 2,2'-biselenopyran; 2,2',2"-triselenopyran; 2,2'-bi-1,4-selenazine; 2,2'-bi-1,3,5-selenadiazine; 2,2'-bi-1-benzoselenopyran; and 1,1'-bis(dibenzoselenopyran).

25 Se Valence Stabilizer #11a: Examples of two-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein both binding sites are composed of selenium (usually selenol or selenoether groups) and are not contained in component heterocyclic rings (Se-Se Bidentates) that meet the requirements for use 30 as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diselenacyclobutane ([4]aneSe₂); diselenacyclopentane ([5]aneSe₂); diselenacyclohexane ([6]aneSe₂); diselenacycloheptane ([7]aneSe₂); diselenacyclooctane ([8]aneSe₂); diselenacyclobutene ([4]eneSe₂); diselenacyclopentene ([5]eneSe₂); diselenacyclohexene ([6]eneSe₂); diselenacycloheptene ([7]eneSe₂); diselenacyclooctene ([8]eneSe₂); diselenacyclobutadiene

([4]dieneSe₂); diselenacyclopentadiene ([5]dieneSe₂); diselenacyclohexadiene ([6]dieneSe₂); diselenacycloheptadiene ([7]dieneSe₂); and diselenacyclooctadiene ([8]dieneSe₂).

Se Valence Stabilizer #11b: Examples of three-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of selenium (usually selenol or selenoether groups) and are not contained in component heterocyclic rings (Se-Se Tridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to:

triselenacyclohexane ([6]aneSe₃); triselenacycloheptane ([7]aneSe₃); triselenacyclooctane ([8]aneSe₃); triselenacyclononane ([9]aneSe₃); triselenacyclodecane ([10]aneSe₃); triselenacycloundecane ([11]aneSe₃); triselenacyclododecane ([12]aneSe₃); triselenacyclohexene ([6]eneSe₃); triselenacycloheptene ([7]eneSe₃); triselenacyclooctene ([8]eneSe₃); triselenacyclononene ([9]eneSe₃); triselenacyclodecene ([10]eneSe₃); triselenacycloundecene ([11]eneSe₃); triselenacyclododecene ([12]eneSe₃); triselenacyclohexatriene ([6]trieneSe₃); triselenacycloheptatriene ([7]trieneSe₃); triselenacyclooctatriene ([8]trieneSe₃); triselenacyclononatriene ([9]trieneSe₃); triselenacyclodecatriene ([10]trieneSe₃); triselenacycloundecatriene ([11]trieneSe₃); and triselenacyclododecatriene ([12]trieneSe₃).

Se Valence Stabilizer #11c: Examples of four-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all binding sites are composed of selenium (usually selenol or selenoether groups) and are not contained in component heterocyclic rings (Se-Se Tetradentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to:

tetraselenacyclooctane ([8]aneSe₄); tetraselenacyclononane ([9]aneSe₄); tetraselenacyclodecane ([10]aneSe₄); tetraselenacycloundecane ([11]aneSe₄); tetraselenacyclododecane ([12]aneSe₄); tetraselenacyclotridecane ([13]aneSe₄); tetraselenacyclotetradecane ([14]aneSe₄); tetraselenacyclopentadecane ([15]aneSe₄); tetraselenacyclohexadecane ([16]aneSe₄); tetraselenacycloheptadecane ([17]aneSe₄); tetraselenacyclooctadecane ([18]aneSe₄); tetraselenacyclononadecane ([19]aneSe₄); tetraselenacycloicosane ([20]aneSe₄); tetraselenacyclooctadiene ([8]dieneSe₄); tetraselenacyclononadiene ([9]dieneSe₄); tetraselenacyclodecadiene ([10]dieneSe₄); tetraselenacycloundecadiene ([11]dieneSe₄);

tetraselenacyclododecadiene ([12]dieneSe₄); tetraselenacyclotridecadiene ([13]dieneSe₄);
tetraselenacyclotetradecadiene ([14]dieneSe₄); tetraselenacyclopentadecadiene ([15]dieneSe₄);
tetraselenacyclohexadecadiene ([16]dieneSe₄); tetraselenacycloheptadecadiene ([17]dieneSe₄);
tetraselenacyclooctadecadiene ([18]dieneSe₄); tetraselenacyclononadecadiene ([19]dieneSe₄);
5 tetraselenacycloicosadiene ([20]dieneSe₄); tetraselenacyclooctatetraene ([8]tetradieneSe₄);
tetraselenacyclononatetraene ([9]tetradieneSe₄); tetraselenacyclodecatetraene
([10]tetradieneSe₄); and tetraselenacycloundecatetraene ([11]tetradieneSe₄).

Se Valence Stabilizer #11d: Examples of six-membered macrocyclics, macrobicyclics, and
10 macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all
binding sites are composed of selenium (usually selenol or selenoether groups) and are not
contained in component heterocyclic rings (Se-Se Tridentates, Se-Se Tetridentates, or Se-Se
Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴
include, but are not limited to: hexaselenacyclododecane ([12]aneSe₆); hexaselenacyclotridecane
15 ([13]aneSe₆); hexaselenacyclotetradecane ([14]aneSe₆); hexaselenacyclopentadecane
([15]aneSe₆); hexaselenacyclohexadecane ([16]aneSe₆); hexaselenacycloheptadecane
([17]aneSe₆); hexaselenacyclooctadecane ([18]aneSe₆); hexaselenacyclononadecane
([19]aneSe₆); hexaselenacycloicosane ([20]aneSe₆); hexaselenacycloheneicosane ([21]aneSe₆);
hexaselenacyclodocosane ([22]aneSe₆); hexaselenacyclotricosane ([23]aneSe₆);
20 hexaselenacyclotetracosane ([24]aneSe₆); hexaselenacyclododecatriene ([12]trieneSe₆);
hexaselenacyclotridecatriene ([13]trieneSe₆); hexaselenacyclotetradecatriene ([14]trieneSe₆);
hexaselenacyclopentadecatriene ([15]trieneSe₆); hexaselenacyclohexadecatriene ([16]trieneSe₆);
hexaselenacycloheptadecatriene ([17]trieneSe₆); and hexaselenacyclooctadecatriene
([18]trieneSe₆).

Se Valence Stabilizer #12a: Examples of four-membered macrocyclics, macrobicyclics, and
25 macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all
four binding sites are composed of selenium and are contained in component 5-membered
heterocyclic rings (Se-Se Tetridentates) that meet the requirements for use as “narrow band”
valence stabilizers for Ce⁺⁴ include, but are not limited to: tetraselenophenes;
30 tetraselenaphospholes; tetraoxaselenoles; and tetradiselenoles.

Se Valence Stabilizer #12b: Examples of six-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all six binding sites are composed of selenium and are contained in component 5-membered heterocyclic rings (Se-Se Tridentates or Se-Se Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: hexaselenophenes; hexaselenaphospholes; hexaoxaselenoles; and hexadiselenoles.

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Se Valence Stabilizer #13a: Examples of four-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all four binding sites are composed of selenium and are contained in a combination of 5-membered heterocyclic rings and selenol and selenoether groups (Se-Se Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diselenatetraselenophenes; tetraselenatetraselenophenes; diselenatetradiselenoles; and tetraselenatetradiselenoles.

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Se Valence Stabilizer #13b: Examples of six-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all six binding sites are composed of selenium and are contained in a combination of 5-membered heterocyclic rings and selenol or selenoether groups (Se-Se Tridentates or Se-Se Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diselenahexaselenophenes; and triselenahexaselenophenes.

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Se Valence Stabilizer #14a: Examples of four-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all four binding sites are composed of selenium and are contained in component 6-membered heterocyclic rings (Se-Se Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: tetraselenopyrans; tetraselenaphosphorins; tetraselenadiphosphorins; tetraoxaselenins; and tetradiselenins.

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Se Valence Stabilizer #14b: Examples of six-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all

six binding sites are composed of selenium and are contained in component 6-membered heterocyclic rings (Se-Se Tridentates or Se-Se Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: hexaselenopyrans; hexaselenaphosphorins; hexaselenadiphosphorins; hexaoxaselenins; and hexadiselenins.

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Se Valence Stabilizer #15a: Examples of four-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all four binding sites are composed of selenium and are contained in a combination of 6-membered heterocyclic rings and selenol or selenoether groups (Se-Se Tetradentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diselenatetraselenopyrans; tetraselenatetraselenopyrans; diselenatetraselenaphosphorins; tetraselenatetraselenaphosphorins; diselenatetraoxaselenins; tetraselenatetraoxaselenins; diselenatetradiselenins; and tetraselenatetradiselenins.

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Se Valence Stabilizer #15b: Examples of six-membered macrocyclics, macrobicyclics, and macropolycyclics (including catapinands, cryptands, cyclidenes, and sepulchrates) wherein all six binding sites are composed of selenium and are contained in a combination of 6-membered heterocyclic rings and selenol or selenoether groups (Se-Se Tridentates, Se-Se Tetradentates, or Se-Se Hexadentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diselenahexaselenopyrans; triselenahexaselenopyrans; diselenahexaselenaphosphorins; triselenahexaselenaphosphorins; diselenahexaoxaselenins; triselenahexaoxaselenins; diselenahexadiselenins; and triselenahexadiselenins.

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Se Valence Stabilizer #16: Examples of 1,3-diselenoketones (diseleno-beta-ketonates), 1,3,5-triselenoketones, bis(1,3-diselenoketones), and poly(1,3-diselenoketones) (Se-Se Bidentates, Se-Se Tridentates, Se-Se Tetradentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: hexafluoropentanediselenone; 1,3-diphenyl-1,3-propanediselenone; selenobenzoyselenopinacolone; diselenocyclohexoxymethane; diphenylpentanetriseleenoate; tetramethylnonanetriseleenoate; hexafluoroheptanetriseleenoate; trifluoroheptanetriseleenoate; 1-(2-thienyl)-1,3-butanediselenone, 1-(2-naphthyl)-1,3-butanediselenone, and trifluoroselenoacetylselenocamphor.

Se Valence Stabilizer #17: Examples of 1,1-diselenolates, bis(1,1-diselenolates), and poly(1,1-diselenolates) (Se-Se Bidentates and Se-Se Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: 1,1-dicyano-2,2-ethylene diselenolate; 1,1-dicarboalkoxy-2,2-ethylene diselenolate; 1,1-di(trifluoromethyl)-2,2-ethylene diselenolate; 1,1-di(pentafluorophenyl)-2,2-ethylene diselenolate; 1-pentamethylene-2,2-ethylene diselenolate; and 1-nitroethylene diselenolate.

Se Valence Stabilizer #18: Examples of diselenocarbamates, bis(diselenocarbamates), and poly(diselenocarbamates) (including N-hydroxydiselenocarbamates and N-mercaptodiselenocarbamates) (Se-Se Bidentates, Se-Se Tridentates, and Se-Se Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: dimethyldiselenocarbamate; di(trifluorodimethyl)diselenocarbamate; diethyldiselenocarbamate; dipropyldiselenocarbamate; diisopropyldiselenocarbamate; dibutyldiselenocarbamate; ditertbutyldiselenocarbamate; dicyanamidodiselenocarbamate; azidoselenoformates; diphenyldiselenocarbamate; di(pentafluorophenyl)diselenocarbamate; dibenzylidiselenocarbamate; dinaphthyldiselenocarbamate; dicyclohexyldiselenocarbamate; dinorbornyldiselenocarbamate; diadamantyldiselenocarbamate; pyrrolidinodiselenocarbamate; piperidinodiselenocarbamate; morpholinodiselenocarbamate; thiamorpholinodiselenocarbamate; 3-pyrrolinodiselenocarbamate; pyrrolodiselenocarbamate; oxazolodiselenocarbamate; isoxazolodiselenocarbamate; thiazolodiselenocarbamate; isothiazolodiselenocarbamate; indolodiselenocarbamate; carbazolodiselenocarbamate; pyrazolinodiselenocarbamate; imidazolinodiselenocarbamate; pyrazolodiselenocarbamate; imidazolodiselenocarbamate; indazolodiselenocarbamate; and triazolodiselenocarbamate.

Se Valence Stabilizer #19: Examples of triselenophosphoric acids (phosphorotriselenoic acids), bis(triselenophosphoric acids), poly(triselenophosphoric acids), and derivatives thereof (Se-Se Bidentates, Se-Se Tridentates, Se-Se Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: triselenophosphoric acid, O-phenyltriselenophosphoric acid, O-benzyltriselenophosphoric acid, O-cyclohexyltriselenophosphoric acid, O-norbornyltriselenophosphoric acid, O,Se-

diphenyltriselenophosphoric acid, O,Se-dibenzyltriselenophosphoric acid, O,Se-dicyclohexyltriselenophosphoric acid, and O,Se-dinorbornyltriselenophosphoric acid.

Se Valence Stabilizer #20: Examples of diselenophosphoric acids (phosphorodiselenoic acids),
5 bis(diselenophosphoric acids), poly(diselenophosphoric acids), and derivatives thereof (Se-Se Bidentates, Se-Se Tridentates, Se-Se Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: diselenophosphoric acid, O-phenyldiselenophosphoric acid, O-benzyldiselenophosphoric acid, O-cyclohexyldiselenophosphoric acid, O-norbornyldiselenophosphoric acid, O,O-diphenyldiselenophosphoric acid, O,O-dibenyldiselenophosphoric acid, O,O-dicyclohexyldiselenophosphoric acid, and O,O-dinorbornyldiselenophosphoric acid.
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Se Valence Stabilizer #21: Examples of tetraselenophosphoric acids (phosphorotetraselenoic acids), bis(tetraselenophosphoric acids), poly(tetraselenophosphoric acids), and derivatives thereof (Se-Se Bidentates, Se-Se Tridentates, Se-Se Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to:
15 tetraselenophosphoric acid, Se-phenyltetraselenophosphoric acid, Se-benzyltetraselenophosphoric acid, Se-cyclohexyltetraselenophosphoric acid, Se-norbornyltetraselenophosphoric acid, Se,Se-diphenyltetraselenophosphoric acid, Se,Se-dibenzyltetraselenophosphoric acid, Se,Se-dicyclohexyltetraselenophosphoric acid, and Se,Se-dinorbornyltetraselenophosphoric acid.
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Se Valence Stabilizer #22: Examples of diselenocarbonates, triselenocarbonates, bis(diselenocarbonates), and bis(triselenocarbonates), (Se-Se Bidentates and S-S Tetridentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: Se,Se-diethyldiselenocarbonate; Se,Se-diisopropylselenocarbonate; Se,Se-diphenyldiselenocarbonate; Se,Se-dibenzyldiselenocarbonate; Se,Se-dicyclohexyldiselenocarbonate; Se,Se-dinorbornyldiselenocarbonate; diethyltriselenocarbonate; diisopropyltriselenocarbonate; diphenyltriselenocarbonate; dibenzyltriselenocarbonate; dicyclohexyltriselenocarbonate; and dinorbornyltriselenocarbonate.
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Se Valence Stabilizer #23: Examples of selenocyanate ligands (Se monodentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: selenocyanate (-SeCN).

5 Se Valence Stabilizer #24: Examples of selenolates (Se monodentates) that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: selenophenol; and naphthaleneselenol.

10 Miscellaneous Valence Stabilizer #1: Examples of diene, bicyclic and tricyclic hydrocarbon ligands that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: cyclopentadiene; azulene; carotene; norbornane; and adamantine.

15 Miscellaneous Valence Stabilizer #2: Examples of cyanide and related ligands that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: cyanide (-CN); and fulminate (-CNO).

Miscellaneous Valence Stabilizer #3: Examples of carbonyl ligands that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: carbonyl (-CO); and carbon dioxide (CO₂) ligands.

20 Miscellaneous Valence Stabilizer #4: Examples of halogens that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: fluorine; chlorine; bromine; and iodine.

25 Miscellaneous Valence Stabilizer #5: Examples of hydroxo and oxo functionalities that meet the requirements for use as “narrow band” valence stabilizers for Ce⁺⁴ include, but are not limited to: water (H₂O); dioxygen (O₂); oxide (O²⁻); hydroxide (OH⁻); peroxy groups (O₂²⁻); and superoxo groups (O₂⁻).

As discussed above, the properties of a particular Ce⁺⁴-containing complex can be altered by changing the substituent groups on these general classes of valence stabilizers. This can influence the effectiveness of corrosion inhibition normally achieved using that specific complex.

5

4e) Mixed Inorganic/Organic Valence Stabilizers

Mixing inorganic and organic valence stabilizers in a conversion coating solution will often result in a coating with poor corrosion-inhibiting properties because of cross interference. Inorganic and organic stabilizers interact with Ce⁺⁴ in different ways. For example, inorganic 10 valence stabilizers will perform their function by forming a shell of octahedrally or icosahedrally coordinated anionic species around a captured Ce⁺⁴ ion. Therefore, the net charge of these inorganic Ce⁺⁴-stabilizer complexes is always negative. Organic species stabilize by the formation of a “hard bond” between the bonding atom in the stabilizer (e.g., nitrogen or oxygen) and the Ce⁺⁴ ion. The net charge of these complexes is often positive. If these two very different 15 types of stabilization ligands are combined, then the magnitude of the charge on the stabilized complex can be reduced significantly. The performance of organic or inorganic stabilized corrosion inhibitor complexes has been found to be directly related to the ability of the complex to form and sustain a thick electrostatic barrier layer. Additionally, a mixed stabilizer can have a poorly developed electrostatic field and a non-optimal packing around the Ce⁺⁴ ion, resulting in a 20 complex with less resistance to aqueous attack. Mixed organic/inorganic stabilized Ce⁺⁴ coatings will generally perform more poorly than coatings that have exclusively organic or inorganic valence stabilizers for this reason.

4f) Valence Stabilizers for Tetraivalent Praseodymium and Terbium

The PrIV and TbIV ions form very few stable complexes with inorganic or organic 25 compounds. Examples of typical wide band inorganic ligands for PrIV and TbIV include periodates, tellurates, tungstates, molybdates, vanadates, carbonates, and phosphates. Under certain circumstances, narrow band inorganic ligands such as oxygen, fluorides, antimonates, iodates, and bromates may be acceptable. Examples of typical organic ligands for PrIV and 30 TbIV include dithiocarbamates, dithiolenes, dithiols, dithioketones, biguanides, oximes, Schiff

bases, and some azo compounds. PrIV and TbIV may be used in the future with compounds not currently identified.

5 5) Additional Solubility Control Agents

One of the roles of the valence stabilizer is to allow for the formation of a tetravalent cerium, praseodymium, or terbium complex that has a specific solubility range. The anions or cations present in the coating solution may be sufficient to form a Ce⁺⁴-, Pr⁺⁴-, or Tb⁺⁴- containing compound within the conversion coating that exhibits the desired solubility characteristics. However, additional solubility control may be desirable to optimize the performance of the tetravalent cerium-, tetravalent praseodymium-, or tetravalent terbium-valence stabilizer complex. The use of an additional solubility control agent is optional, not required.

15 Both the organic and inorganic valence stabilizers described above may need some kind of additional solubility control that can be in the form of either inorganic or organic compounds. The key to selecting solubility control agents is to match the cationic or anionic modifiers with individual Ce⁺⁴-, Pr⁺⁴-, or Tb⁺⁴-valence stabilizer combinations. Some cations or anions may work to optimize one Ce⁺⁴-, Pr⁺⁴-, or Tb⁺⁴-valence stabilizer complex, but this does not necessarily mean they will optimize the solubility of a different complex.

20 The initial formation of a conversion coating may produce Ce⁺⁴, Pr⁺⁴, or Tb⁺⁴ compounds with solubilities greater than optimal. A post-deposition treatment can be applied to the coating as a remedial treatment or as a desired process step. Additional solubility control agents applied to a work piece can enhance the Ce⁺⁴, Pr⁺⁴, or Tb⁺⁴ content of the coating by forming more insoluble compounds in place. Application of a second solution after the conversion coating 25 process has been found to result in enhanced solubility control of Ce⁺⁴, Pr⁺⁴, or Tb⁺⁴ in the conversion coating.

30 Additional solubility control agents are typically applied as a second solution. Otherwise, these cations or anions would begin to precipitate cerium-, praseodymium-, or terbium-containing compounds in the conversion coating solution, depleting it of cerium, praseodymium, or terbium prior to treating the work piece. In general, fine tuning of solubility by cationic species is typical for Ce⁺⁴-, Pr⁺⁴-, or Tb⁺⁴-stabilizer combinations when an inorganic valence stabilizer is used, and by anionic species when an organic valence stabilizer is used.

The need for an additional solubility control agent may be illustrated for the situation where molybdate is used as a valence stabilizer for a Ce⁺⁴ conversion coating. Cationic species are necessary to deposit a Ce⁺⁴/molybdate complex within the coating (the net charge on a Ce⁺⁴/heteropoly(molybdate) anion may either be -2, -4, or -8). The cationic species needed to balance the charge and form a compound is usually supplied from cations already present in the conversion coating solution and/or by cations being pulled into the solution from the work piece. However, if the Ce⁺⁴/molybdate complex composed of the available cations has a much greater solubility than desired, then additional solubility control agents can be employed. The differences in effectiveness of conversion coatings on various alloy compositions is likely a reflection of the influence that the composition of the alloy itself has on the solubility of the deposited conversion coating. Similarly, anions present in a conversion coating solution or source material will be incorporated in a Ce⁺⁴ compound that requires a negative charge balance. This is frequently observed with Ce⁺⁴/organic valence stabilizer combinations.

Additional solubility control can be achieved through the use of non-toxic inorganic cations which include, but are not limited to: H⁺, Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, NH₄⁺, Mg⁺², Ca⁺², Sr⁺², Y⁺³, La⁺³, Ce⁺³, Ce⁺⁴, Nd⁺³, Pr⁺³, Sc⁺³, Sm⁺³, Eu⁺³, Eu⁺², Gd⁺³, Tb⁺³, Dy⁺³, Ho⁺³, Er⁺³, Tm⁺³, Yb⁺³, Lu⁺³, Ti⁺⁴, Zr⁺⁴, Ti⁺³, Hf⁺⁴, Nb⁺⁵, Ta⁺⁵, Nb⁺⁴, Ta⁺⁴, Mo⁺⁶, W⁺⁶, Mo⁺⁵, W⁺⁵, Mo⁺⁴, W⁺⁴, Mn⁺², Mn⁺³, Mn⁺⁴, Fe⁺², Fe⁺³, Co⁺², Co⁺³, Ru⁺², Ru⁺³, Ru⁺⁴, Rh⁺³, Ir⁺³, Rh⁺², Ir⁺², Pd⁺⁴, Pt⁺⁴, Pd⁺², Pt⁺², Cu⁺, Cu⁺², Cu⁺³, Ag⁺, Ag⁺², Ag⁺³, Au⁺, Au⁺², Au⁺³, Zn⁺², Al⁺³, Ga⁺³, Ga⁺, In⁺³, In⁺, Ge⁺⁴, Ge⁺², Sn⁺², Sn⁺⁴, Sb⁺³, Sb⁺⁵, Bi⁺³, and Bi⁺⁵. Any water-soluble compound that contains these cations can be used for this purpose. Nitrates, chlorides, bromides, and perchlorates of these cations offer inexpensive water-soluble precursors, although many other water-soluble precursors exist.

Cationic solubility control may also be achieved through the use of nontoxic organic cations that include, but are not limited to: quaternary ammonium compounds (NR₄⁺, where R can be any combination of alkyl, aromatic, or acyclic organic substituents, such as the methyltriethylammonium ion); organics that contain at least one N⁺ site (such as pyridinium or thiazolium cations); organics that contain at least one phosphonium site (P⁺, such as the benzyltriphenylphosphonium ion); organics that contain at least one stibonium site (Sb⁺, such as the tetraphenylstibonium ion); organics that contain at least one oxonium site (O⁺, such as pyrylium cations); organics that contain at least one sulfonium site (S⁺, such as the

triphenylsulfonium ion); and organics that contain at least one iodonium site (I^+ , such as the diphenyliodonium ion).

The quaternary ammonium compounds, organics containing at least one N^+ site, and organics containing at least one oxonium site are the most important of these classifications 5 because of the very large number of stable cations that are available. Water-soluble precursors for these organic cations are desirable in order to maximize the amount of material available in the appropriate conversion coating solution. Fluorides, chlorides, and bromides offer the most water-soluble precursors for these organic cations, although lower molecular weight nitrates and perchlorates of these cations (e.g., tetramethylammonium) are also acceptable water-soluble 10 precursors. Larger molecular weight nitrates and perchlorates are not generally acceptable as precursors because of their low water solubility.

Although it is less desirable, toxic inorganic or organic cations can be used as additional 15 solubility control agents. Examples of toxic inorganic cations that can be used include, but are not limited to: Be^{+2} , Ba^{+2} , V^{+5} , V^{+4} , V^{+3} , Cr^{+3} , Ni^{+2} , Ni^{+4} , Os^{+4} , Cd^{+2} , Hg^{+1} , Hg^{+2} , Tl^+ , Tl^{+3} , As^{+3} , As^{+5} , Pb^{+2} , and Pb^{+4} . Examples of toxic organic cations include, but are not limited to: organic 20 compounds that contain at least one arsonium site (As^+ , an example being the tetraphenylarsonium ion) and organic compounds that contain at least one selenonium site (Se^+ , an example being the triphenylselenonium ion). Use of these materials for additional solubility control may be desirable in some specific instances where the toxicity of the coating bath is of limited importance to the operator. Water-soluble precursors for these toxic cations are desirable 25 in order to maximize the amount of available cation for solubility control. In general, the nitrates, fluorides, chlorides, bromides, and perchlorates of these cations offer the highest water solubility.

Additional solubility control can also be achieved through the use of nontoxic inorganic 30 anions, especially for $Ce^{+4}/$, $Pr^{+4}/$, or $Tb^{+4}/$ organic valence stabilizer combinations. Water-soluble precursors for these inorganic anions are desirable in order to maximize the amount of material available in the appropriate conversion coating solution. These include, but are not limited to: fluorotitanates, chlorotitanates, fluorozirconates, chlorozirconates, fluoroniobates, chloroniobates, fluorotantalates, chlorotantalates, molybdates, tungstates, permanganates, fluoromanganates, chloromanganates, fluoroferrates, chloroferrates, fluorocobaltates, chlorocobaltates, fluorozincates, chlorozincates, borates, fluoroborates, fluoroaluminates,

chloroaluminates, carbonates, silicates, fluorosilicates, fluorostannates, nitrates, nitrites, azides, phosphates, phosphites, phosphonates, phosphinites, thiophosphates, thiophosphites, thiophosphonates, thiophosphinites, fluorophosphates, fluoroantimonates, chloroantimonates, sulfates, sulfites, sulfonates, thiosulfates, dithionites, dithionates, fluorosulfates, tellurates, 5 fluorides, chlorides, chlorates, perchlorates, bromides, bromates, iodides, iodates, periodates, and heteropolyanions (e.g., heteropolymolybdates, silicomolybdates).

Additional solubility control can also be achieved through the use of an almost unlimited number of non-toxic organic anions (e.g., organics with different carboxylates or acid groups). Examples include, but are not limited to: ferricyanides; ferrocyanides; cyanocobaltates; 10 cyanocuprates; cyanomanganates; cyanates; cyanatoferates; cyanatocobaltates; cyanatocuprates; cyanatomanganates; thiocyanates; thiocyanatoferates; thiocyanatocobaltates; thiocyanatocuprates; thiocyanatomanganates; cyanamides; cyanamidoferates; cyanamidocobaltates; cyanamidocuprates; cyanamidomanganates; nitritoferates; nitritocobaltates; azides; (thio)carboxylates, di(thio)carboxylates, tri(thio)carboxylates, or 15 tetra(thio)carboxylates [useful representatives including, but not limited to, acetic acid, benzoic acid, succinic acid, fumaric acid, salicylic acid, lactic acid, tartaric acid, antimonyl tartrates, cinnamic acid, adipic acid, phthalic acid, terephthalic acid, citric acid, ascorbic acid, malic acid, malonic acid, oxalic acid, stearic acid, gallic acid, naphthenic acid, camphoric acid, nitrosalicylic acid, aminosalicylic acid, acetylsalicylic acid, sulfosalicylic acid, nitrobenzoic acid, perfluoroC₂- 20 16 carboxylic acids, trinitrobenzoic acid, chlorobenzoic acid, anisic acid, iodobenzoic acid, anthranilic acid, mandelic acid, toluic acid, nicotinic acid, isonicotinic acid, pyrazolecarboxylic acid, picrolonic acid, quinaldic acid, diphenic acid, benzoquinaldic acid, quinolinecarboxylic acid, isoquinolinecarboxylic acid, triazinecarboxylic acid, (thio)carbonic acids, (thio)carbamic acids, trimethylhexylic acid, tetrafluorophthalic acid, ethylenediaminetetraacetic acid, 25 toluoylpropionic acid, lactobionic acid, octylthiopropionate, lipoic acid, methylbenzoylpropionic acid, anthracenesuccinic acid, benzothiazolecarboxylic acid, phenylacetic acid, glycolic acid, thioglycolic acid, benzothiazolylthiosuccinic acid, benzothiazolylthiopropionic acid, phenylanthranilic acid, furancarboxylic acid, nitrofuroic acid, phosphonobutanetricarboxylic acid, benzothiazolylthiosuccinic acid, N-phosphonomethylglycine, cresoxyacetic acid, 30 aminobutyric acid, alanine, asparagine, cysteine, glutamine, glycine, leucine, methionine, phenylalanine, proline, serine, threonine, tryptophan, tyrosine, valine, glutamic acid, aspartic

acid, arginine, histidine, lysine, trihydroxyglutaric acid, phenoxyacetic acid, hydroxynaphthoic acid, phenylbutyric acid, hydroxyphosphonoacetic acid, tropic acid, aminophenylpropionic acid, dihydrocinnamic acid, hydroxycinnamic acid, cinchomeronic acid, aurintricarboxylic acid, benzotriazolecarboxylic acid, hydroxyphosphonoacetic acid, cyanuric acid, barbituric acid,
5 violuric acid, diphenylvioluric acid, dilituric acid, thiobarbituric acid, cresotic acid, trimethylhexylic acid, nitrilotriacetic acid, N,N'-terephthaloylbis(aminocaproic acid), ethyleneglycolbis(aminoethyllether)tetraacetic acid, diethylenetriaminepentaacetic acid, 2-phosphonobutanetricarboxylic acid, N,N'-bis(2-hydroxsuccinyl)ethylenediamine, nicotinic acid, naptalam, nitrobenzoic acid, nonylphenoxyacetic acid, and olsalazine]; (thio)phenolates,
10 di(thio)phenolates, tri(thio)phenolates, or tetra(thio)phenolates [useful representatives including, but not limited to, pyrocatechol, resorcinol, picric acid, styphnic acid, pyrogallol, purpurin, purpurogallin, benzopurpurin, gallein, thiophenol, rhodizonic acid, kojic acid, chromotropic acid, carminic acid, fluorescein, tannic acid, and humic acid]; (thio)phosphonates,
15 di(thio)phosphonates, or tri(thio)phosphonates [useful representatives including, but not limited to, diethylphosphonic acid, diphenylphosphonic acid, nitrophenylphosphonic acid, perfluoroC₂-16phosphonic acids, benzenephosphonic acid, phytic acid, hydroxyethylidenebisphosphonic acid, nitrilotrimethylenephosphonic acid, aminomethylenephosphonic acid, etidronic acid, ethylphosphonic acid, chloroethylphosphonic acid, ethylenediaminetetramethylenephosphonic acid, laurylhydroxydiphosphonic acid, methylaminodimethylenephosphonic acid,
20 alkyl(aryl)diphosphonic acids, N-cetylaminoethanedi phosphonic acid, carboxyhydroxymethylphosphonic acid (hpa), oxyethylidenediphosphonic acid, polycaproamidophosphonates, phenylethanetriphosphonic acid, oxidronic acid, and pamidronic acid]; (thio)phosphonamides, di(thio)phosphonamides, or tri(thio)phosphonamides [useful
representatives including, but not limited to, phosphoramidic acid, phosphordiamidic acid
25 (diamidophosphonic acid), and phosphoramidothioic acid]; amino(thio)phosphonates, diamino(thio)phosphonates, or triamino(thio)phosphonates; imino(thio)phosphonates or diimino(thio)phosphonates; (thio)sulfonates, di(thio)sulfonates, or tri(thio)sulfonates [useful
representatives including, but not limited to, methanesulfonic acid, benzenesulfonic acid, aminobenzenesulfonic acid (sulfanilic acid), nitrobenzenesulfonic acid, phenylsulfonic acid,
30 naphthalenesulfonic acid, nitronaphthalenesulfonic acid, oxinesulfonic acid, alizarinsulfonic acid, benzidinesulfonic acid, flavianic acid, camphorsulfonic acid, diiodophenolsulfonic acid

(soziodol), 8-hydroxyquinoline-5-sulfonic acid, 7-nitro-8-hydroxyquinoline-5-sulfonic acid, benzotriazolesulfonic acid, bis(trifluoromethyl)benzenesulfonic acid, diiododihydroxybenzophenonesulfonic acid, p-amino-p'-ethoxydiphenylamine-o-sulfonic acid, 1-amino-2-naphthol-4-sulfonic acid, 1,2-diaminoanthraquinone-3-sulfonic acid, 1,5-dinitro-2-naphthol-7-sulfonic acid, perfluoroC₂₋₁₆sulfonic acids, benzenedisulfonic acid, phenyldisulfonic acid, naphthalenedisulfonic acid, 3,6-naphtholdisulfonic acid, indigodisulfonic acid, benzidinedisulfonic acid, carboxyiodobenzenesulfonic acids, N-benzeneaminomethanesulfonic acid (ams), amido-G-acid, amido-R-acid, naphthalene(di)sulfonic acid (Armstrong's acid), amsonic acid, Badische acid, camphorsulfonic acid, chrysophenine, Cassella's acid, chromotropic acid, Cleve's acid, croceic acid, anthracenesulfonic acid, hydroxyquinolinesulfonic acid, hydrazinobenzenesulfonic acid, indigo carmine, indoxyl, isatinsulfonic acid, indican, lignosulfonic acid, metanil yellow, metanilic acid, naphthoquinonesulfonic acid, Nuclear Fast Red, naphthol(di)sulfonic acid, naphthylamine(di)sulfonic acid, Orange I, orthanilic acid, phenol(di)sulfonic acid, methylenediphthalenesulfonic acid, methyl orange, and 15 piperazinediethanesulfonic acid (pipes)]; (thio)sulfonamides, di(thio)sulfonamides, or tri(thio)sulfonamides; amino(thio)sulfonates, diamino(thio)sulfonates, or triamino(thio)sulfonates; imino(thio)sulfonates (including sulfamates) or diimino(thio)sulfonates (including disulfamates) [useful representatives including, but not limited to, methylsulfamic acid and phenylsulfamic acid]; (thio)borates, di(thio)borates, or (thio)boronates [useful 20 representatives including, but not limited to, phenylboric acid and borotartaric acid]; organic silicates; and stibonates [useful representatives including, but not limited to, antimonyl tartrate and benzenestibonic acid]. Water-soluble precursors for these organic anions are desirable to maximize the amount available in the appropriate conversion coating solution.

Finally, toxic inorganic or organic anions can be used as additional solubility control 25 agents, although this is less desirable. Examples of toxic inorganic anions include, but are not limited to: arsenates, arsenites, fluoroarsenates, chloroarsenates, selenates, selenites, fluorothallates, chlorothallates, iodomercury anions (e.g., Nessler's reagent), thiocyanatomercury anions (e.g., Behren's reagent), chloromercurates, bromomercurates, osmates, fluoronickelates, chromates, Reinecke's salt, and vanadates. Examples of toxic organic anions include cyanides; 30 cyanochromates; cyanonickelates; cyanatochromates; cyanatonickelates; thiocyanatochromates; thiocyanatonickelates; cyanamidochromates; cyanamidonickelates; nitritonickelates; arsonates,

diarsonates, or triarsonates [useful representatives including, but not limited to, propylarsonic acid, phenylarsonic acid, hydroxyphenylarsonic acid, benzeneearsonic acid, methylbenzeneearsonic acid, hydroxybenzeneearsonic acid, and nitrobenzeneearsonic acid]; organic selenates, diselenates, or triselenates. These materials may be necessary in some specific instances for additional solubility control where coating bath toxicity is of limited importance.

5 Water-soluble precursors for these anions are desirable in order to maximize the amount of available anion to interact with the Ce⁺⁴, Pr⁺⁴, or Tb⁺⁴ complex. The alkali or ammonium species of these anions typically offer the greatest water solubility.

10 6) Agents to Increase Color-Fastness of Coating

Conversion coatings will frequently be colored to improve the aesthetic nature of the work piece, as well as to aid in the identification of coated versus uncoated areas. Long-term exposure to high energy wavelengths (i.e., the ultraviolet wavelengths of sunlight) may fade or dim the color of the coated work piece. The conversion coating solution may include agents that 15 improve the color-fastness of the coating. Typically, these are termed “UV blockers” in the paint and coatings literature. Active UV blockers are typically dark in color and function by absorbing nearly all of the light energy. Passive UV blockers are light in color and function by reflecting back nearly all of the light energy. Examples of active UV blockers include carbon black, graphite and phthalocyanines. Examples of passive UV blockers include titanium oxide, tin 20 oxide, silicon oxide, silicates, or aluminosilicates.

7) Agents to Add Color to the Formed Coating

It is desirable that coatings placed directly onto metal work pieces be colored so as to provide a metric of coating thickness, to identify uncoated areas, or even for aesthetic purposes. 25 Rare earth compounds often exhibit no color in the coating, or result in very pale colored coatings. For this reason, it may optionally be advantageous to add a solvent-soluble (typically water-soluble) colorant to the conversion coating solution. Dye chemicals such as vat dyes (i.e., indigo or anthraquinone), mordant and lake dyes (i.e., alizarin), direct dyes (i.e., mauve), disperse dyes (i.e., quinones), azo dyes, triazene dyes, triphenylmethane dyes (i.e., malachite 30 green), azine dyes (i.e., methylene blue), formazan dyes, phthalocyanine dyes, Schiff Base dyes, or naturally-occurring dyes (such as anthocyanins, carotenoids, quinines, melanins,

omnochromes, pterins, porphyrins, and indigoids), or combinations thereof, can be used for this purpose. Inorganic pigments are also acceptable.

B. SOLUTION COMPOSITION AND PREPARATION

5 Additional important process considerations include chemical concentrations, pH of the coating solution, redox potential of the coating solution, application temperature, and contact time.

10 **1) Solvents**

Water is a typical solvent for these conversion coating solutions due to its availability and low cost. Other solvents or combinations of water with other solvents (such as alcohols, ketones, etc.) may also be used if desired. However, these processes will be more costly than those using water exclusively.

15 **2) Cerium, Praseodymium, or Terbium Concentration**

The maximum concentration of the cerium, praseodymium, or terbium source depends upon the solubility of the specific source used. Any concentration exceeding this precursor solubility will result in undissolved solid material that will not be incorporated into the conversion coating and may even act as flaws in the coating. The ambient temperature processes outlined here produce Ce^{+4} , Pr^{+4} , or Tb^{+4} conversion coatings with exceptional corrosion-inhibiting character. Therefore, the solubility of the cerium, praseodymium, or terbium sources in water at or near ambient temperature ($25^{\circ}C$) should be the maximum amount of the cerium, praseodymium, or terbium source that is added. Since the solubility of virtually all materials in water increases with temperature, more cerium, praseodymium, or terbium can be added to the conversion coating solution if the temperature of the bath is increased from ambient. Although higher temperatures lead to higher allowable concentrations of cerium, praseodymium, or terbium precursors, this is unnecessary and adds to the cost of the process.

30 Acidic pHs will typically increase the solubility of many inorganic materials, thereby increasing the concentration of cerium, praseodymium, or terbium available in solution. A general estimate of the maximum concentration of cerium or praseodymium in the conversion coating solution at ambient conditions can be determined from the solubilities of some of the

more desirable cerium or praseodymium sources listed in Table 3. The solubility of terbium sources is often comparable to praseodymium sources.

Table 3
Solubilities of Some Cerium and Praseodymium Sources under Ambient Conditions
[Maximum Concentration of Cerium or Praseodymium in Solution]
(at or near 25°C and at or near pH 7)

Cerium or Praseodymium Source	Solubility in Water (mole/L)
Cerium (III) nitrate	1.5×10^0
Cerium (III) sulfate	1.2×10^{-1}
Cerium (III) perchlorate	2.0×10^0
Cerium (III) chloride	4.1×10^0
Cerium (III) bromide	1.0×10^0
Cerium (III) iodide	1.0×10^{-1}
Cerium (III) bromate	1.0×10^0
Cerium (III) formate	1.3×10^{-2}
Cerium (III) acetate	6.6×10^{-1}
Cerium (III) propionate	4.6×10^{-1}
Cerium (III) butyrate	7.7×10^{-2}
Cerium (III) dimethylphosphate	7.6×10^{-1}
Ammonium cerium (III) nitrate	5.7×10^0
Magnesium cerium (III) nitrate	4.3×10^{-1}
Ammonium cerium (III) sulfate	7.0×10^{-2}
Cerium (IV) chloride	1.0×10^0
Cerium (IV) perchlorate	1.0×10^0
Cerium (IV) sulfate	5.0×10^{-1}
Cerium (IV) nitrate	1.0×10^0
Cerium (IV) acetate	5.0×10^{-1}
Ammonium cerium (IV) nitrate	2.6×10^0

Ammonium cerium (IV) sulfate	5.0×10^{-1}
Praseodymium (III) nitrate	1.4×10^0
Praseodymium (III) sulfate	3.1×10^{-1}
Praseodymium (III) perchlorate	2.2×10^0
Praseodymium (III) chloride	8.9×10^0
Praseodymium (III) bromide	1.0×10^{-1}
Praseodymium (III) iodide	1.0×10^0
Praseodymium (III) bromate	2.9×10^0
Praseodymium (III) acetate	6.3×10^{-1}
Magnesium praseodymium (III) nitrate	4.1×10^{-1}

5 The depletion of cerium, praseodymium, or terbium from the coating solution below an acceptable level is a function of the amount of metal surface area being coated prior to regeneration of the solution. A coating applied to a very large surface area may deplete the solution to the point that subsequent solution applications no longer form effective coatings. Less cerium, praseodymium, or terbium will be removed from the conversion coating solution
10 when treating a smaller surface area of metal, so more work pieces can be coated from the same solution.

15 The corrosion-inhibiting cerium, praseodymium, or terbium compounds formed on the surface of the metal exhibit solubilities ranging from approximately 5×10^{-2} to 5×10^{-5} moles/liter of cerium, praseodymium, or terbium in water. Coating solutions with cerium, praseodymium, or terbium concentrations much less than these concentrations may: 1) withdraw cerium, praseodymium, or terbium from the formed coating in order to attempt to reach an equilibrium, or 2) may produce an incomplete, poorly formed oxide film. Intentionally exhausted (depleted) conversion coating solutions have been observed to degrade a coated surface and return cerium, praseodymium, or terbium to the coating solution. The lowest concentration of cerium, praseodymium, or terbium in the precursor conversion coating bath
20 from which some resultant corrosion inhibition will be exhibited is probably in the range of 1×10^{-3} to 1×10^{-4} moles/liter of cerium, praseodymium, or terbium. We used cerium concentrations of approximately 1×10^{-1} mole/liter of cerium with excellent results.

3) Oxidizer Concentration

The concentration of the oxidizer source can range up to the maximum solubility of the specific oxidizer source used. Any concentration exceeding this solubility will result in undissolved solid material that will not be available to raise the redox potential of the conversion coating solution. This process is designed to operate at ambient temperatures, so the maximum concentration of oxidizer source should be restricted to its maximum solubility in water at or near ambient temperature (25°C). As discussed above, more oxidizer can be added to the conversion coating solution if the temperature of the bath is increased from ambient. Higher temperatures may lead to higher allowable concentrations of oxidizer precursors, but this is unnecessary and undesirable in light of process economics. Table 4 shows the solubilities in water of some of the more desirable oxidizer sources.

Table 4
Solubilities of Some Oxidizer Sources under Ambient Conditions
(At or near 25°C and at or near pH 7)

Oxidizer Source	Example Precursor	Solubility in Water (mole/L)
A) Peroxides and Superoxides	Hydrogen peroxide Lithium peroxide Sodium peroxide Potassium superoxide	60 wt. % 1×10^0 1×10^0 1×10^0
B) Persulfates	Ammonium persulfate Lithium persulfate Sodium persulfate Potassium persulfate Magnesium persulfate Calcium persulfate Strontium persulfate Barium persulfate	2.6×10^0 3×10^0 3.1×10^0 2.0×10^{-1} 1×10^1 1×10^1 5×10^0 1.3×10^0
C) Perborates	Ammonium perborate Lithium perborate Sodium perborate Potassium perborate	1.8×10^{-1} 1×10^{-1} 1.7×10^{-1} 1.1×10^{-1}
D) Peroxybenzoates	Monoperoxyphthalic acid Magnesium monoperoxyphthalate Chloroperoxybenzoic acid	1×10^1 1×10^1 1×10^1

E) Chlorites	Lithium chlorite Sodium chlorite Calcium chlorite Strontium chlorite Barium chlorite	5×10^0 4.3×10^0 1×10^0 5×10^{-1} 1×10^{-1}
F) Bromates	Ammonium bromate Lithium bromate Sodium bromate Potassium bromate Rubidium bromate Cesium bromate Magnesium bromate Calcium bromate Strontium bromate Zinc bromate Ferric bromate	1×10^1 4.85×10^0 1.82×10^0 8.0×10^{-1} 1.4×10^{-1} 1.4×10^{-1} 1.0×10^0 1×10^0 9.1×10^{-1} 1×10^0 $\sim 1 \times 10^0$
G) Hypochlorites	Lithium hypochlorite Sodium hypochlorite Magnesium hypochlorite Calcium hypochlorite Strontium hypochlorite Barium hypochlorite	1×10^1 1×10^1 1×10^1 1×10^1 5×10^0 5×10^0
H) Periodates	Periodic acid Ammonium periodate Lithium periodate Sodium periodate Potassium periodate Rubidium periodate Cesium periodate Magnesium periodate	4.96×10^1 1.3×10^{-1} 1×10^0 6.7×10^{-1} 2.9×10^{-2} 2.4×10^{-2} 6.6×10^{-2} 1×10^{-2}
I) Permanganates	Ammonium permanganate Lithium permanganate Sodium permanganate Potassium permanganate Magnesium permanganate Calcium permanganate Strontium permanganate Barium permanganate Zinc permanganate Ferric permanganate	5.77×10^{-1} 3.97×10^0 1×10^0 4.04×10^{-1} 1×10^1 9.18×10^0 7.67×10^0 2.01×10^0 8.10×10^{-1} $\sim 1 \times 10^0$
J) Chlorates	Lithium chlorate Sodium chlorate Potassium chlorate Rubidium chlorate Cesium chlorate Magnesium chlorate Calcium chlorate Strontium chlorate Zinc chlorate Barium chlorate	5.5×10^1 7.5×10^0 5.8×10^{-1} 3.0×10^{-1} 2.9×10^{-1} 4.3×10^0 7.4×10^0 6.9×10^0 8.6×10^0 8.5×10^{-1}

K) Perchlorates	Perchloric acid Ammonium perchlorate Lithium perchlorate Sodium perchlorate Potassium perchlorate Rubidium perchlorate Cesium perchlorate Magnesium perchlorate Calcium perchlorate Strontium perchlorate Zinc perchlorate Barium perchlorate Aluminum perchlorate Ferric perchlorate Tetramethylammonium perchlorate Tetraethylammonium perchlorate Tetrapropylammonium perchlorate	75 wt. % 1.3×10^0 5.6×10^0 1.5×10^1 3.6×10^{-1} 2.2×10^{-1} 8.6×10^{-2} 4.4×10^0 7.9×10^0 1.1×10^1 $\sim 1 \times 10^0$ 5.1×10^0 $\sim 1 \times 10^0$ $\sim 1 \times 10^0$ $\sim 5 \times 10^{-1}$ $\sim 1 \times 10^{-1}$
L) Nitrates	Nitric acid Ammonium nitrate Lithium nitrate Sodium nitrate Potassium nitrate Rubidium nitrate Cesium nitrate Magnesium nitrate Calcium nitrate Strontium nitrate Zinc nitrate Barium nitrate Aluminum nitrate Ferric nitrate Tetramethylammonium nitrate Tetraethylammonium nitrate Tetrapropylammonium nitrate Tetrabutylammonium nitrate	75 wt. % 2.5×10^1 1.3×10^1 1.1×10^1 7.4×10^0 3.0×10^0 2.1×10^0 4.9×10^0 2.1×10^1 3.4×10^0 6.2×10^0 3.3×10^{-1} 1.7×10^0 5.7×10^0 $\sim 1 \times 10^1$ $\sim 5 \times 10^0$ $\sim 1 \times 10^0$ $\sim 5 \times 10^{-1}$
M) Nitrites	Lithium nitrite Sodium nitrite Potassium nitrite Magnesium nitrite Calcium nitrite Strontium nitrite Zinc nitrite Barium nitrite	2.8×10^1 1.3×10^1 3.5×10^1 $\sim 1 \times 10^0$ 3.9×10^0 3.8×10^0 $\sim 1 \times 10^0$ 2.9×10^0
N) Vanadates	Vanadium pentoxide Ammonium vanadate Lithium vanadate Sodium vanadate Potassium vanadate Magnesium vanadate Calcium vanadate	4.4×10^{-2} 4.4×10^{-2} $\sim 1 \times 10^0$ 1.7×10^0 $\sim 1 \times 10^0$ $\sim 1 \times 10^0$ $\sim 5 \times 10^{-1}$

O) Iodates	Iodic acid Iodine pentoxide Ammonium iodate Lithium iodate Sodium iodate Potassium iodate Magnesium iodate	1.76×10^1 5.6×10^0 1×10^{-1} 4.4×10^0 4.5×10^{-1} 2.2×10^{-1} 2.3×10^{-1}
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15 Low oxidizer concentrations may not oxidize a sufficient quantity of cerium, praseodymium, or terbium from the trivalent state to the tetravalent state. This would result in reduced corrosion-inhibiting performance. The net redox potential of the coating solution is also a function of the surface area of the metal that has been coated. The redox potential decreases over time (e.g., several days), so these solutions typically need additions of oxidizer to maintain the redox potential.

20

4) Preparative Agent Concentration

25 The concentration of the preparative agent is desirable for the conversion coating process. Cratering of the coated metal surface has been found when the solution concentration of the preparative agent exceeds (or even approaches) the solubility of the precursor material. This cratering results in coatings with reduced corrosion resistance. Solubility values for many fluorides (a typical preparative agent) are given in Table 5. The added concentrations should not exceed (or come close to) these values. Of course, variations in the solution temperature and pH will change the solubilities of each of these preparative agents, but the values given below can be used as general approximations.

30

Table 5
Solubilities of Fluoride Preparative Agents under Ambient Conditions
[Maximum Allowable Concentrations in Solution]
(At or near 25°C and at near pH 7)

Fluoride Source	Example Precursor	Solubility in Water (mole/L)
A) Simple Fluorides	Hydrofluoric acid	75 wt. %
	Ammonium fluoride	2.7×10^1
	Lithium fluoride	1.04×10^{-1}
	Sodium fluoride	1.01×10^0
	Potassium fluoride	1.59×10^1
	Potassium bifluoride	5.25×10^0
	Rubidium fluoride	1.25×10^1
	Cesium fluoride	2.42×10^1
	Copper (II) fluoride	4.62×10^{-1}
	Silver (I) fluoride	1.43×10^1
	Zinc fluoride	1.57×10^{-1}
	Aluminum fluoride	6.6×10^{-2}
	Titanium fluoride	1×10^0
	Zirconium fluoride	8.3×10^{-2}
	Germanium fluoride hydrate	1×10^{-1}
	Tin (II) fluoride	1×10^{-1}
	Tin (IV) fluoride	1×10^0
	Vandium fluoride	1×10^{-1}
	Niobium fluoride	1×10^0
	Tantalum fluoride	1×10^{-1}
	Antimony (III) fluoride	3.15×10^{-1}
	Antimony (V) fluoride	1×10^{-1}
	Manganese (II) fluoride	7.1×10^{-2}
	Cobalt (II) fluoride	1.55×10^{-1}
B) Hexafluorozirconates	Ammonium hexafluorozirconate	1×10^{-1}
	Lithium hexafluorozirconate	8×10^{-2}
	Sodium hexafluorozirconate	6×10^{-2}
	Potassium hexafluorozirconate	8.12×10^{-2}
	Rubidium hexafluorozirconate	8.48×10^{-2}
	Cesium hexafluorozirconate	1.12×10^{-1}
C) Hexafluorotitanates	Ammonium hexafluorotitanate	$\sim 1 \times 10^{-1}$
	Lithium hexafluorotitanate	$\sim 5 \times 10^{-2}$
	Sodium hexafluorotitanate	$\sim 1 \times 10^{-2}$
	Potassium hexafluorotitanate	6.0×10^{-2}
	Rubidium hexafluorotitanate	2.5×10^{-2}
	Cesium hexafluorotitanate	5.5×10^{-2}

D) Hexafluorosilicates	Ammonium hexafluorosilicate Lithium hexafluorosilicate Sodium hexafluorosilicate Potassium hexafluorosilicate Rubidium hexafluorosilicate Cesium hexafluorosilicate Silver (I) hexafluorosilicate Magnesium hexafluorosilicate Calcium hexafluorosilicate Strontium hexafluorosilicate Zinc hexafluorosilicate Copper (II) hexafluorosilicate Cobalt (II) hexafluorosilicate Manganese (II) hexafluorosilicate Iron (II) hexafluorosilicate Iron (III) hexafluorosilicate	1.04×10^0 3.8×10^0 3.5×10^{-2} 5.5×10^{-3} 6.9×10^{-3} 2.3×10^{-2} 1×10^{-0} 3.9×10^0 1×10^{-1} 1.2×10^{-1} 1×10^0 7.4×10^0 3.82×10^0 4.59×10^0 4.19×10^0 4.19×10^0
E) Hexafluoroaluminates	Ammonium hexafluoroaluminate Lithium hexafluoroaluminate Sodium hexafluoroaluminate Potassium hexafluoroaluminate	5.3×10^{-2} 6.6×10^{-3} 2.9×10^{-3} 6.1×10^{-3}
F) Tetrafluoroborates	Ammonium tetrafluoroborate Lithium tetrafluoroborate Sodium tetrafluoroborate Potassium tetrafluoroborate	2.4×10^0 1×10^0 9.8×10^0 3.5×10^{-2}
G) Hexafluorogermanates	Ammonium hexafluorogermanates Potassium hexafluorogermanates Rubidium hexafluorogermanates Cesium hexafluorogermanates	1×10^{-1} 2.0×10^{-2} 1×10^{-2} 1×10^{-2}
H) Hexafluorostannates	Ammonium hexafluorostannate Lithium hexafluorostannate Sodium hexafluorostannate Potassium hexafluorostannate Rubidium hexafluorostannate Cesium hexafluorostannate	1×10^{-1} 1×10^{-2} 1×10^{-2} 1.28×10^{-1} 6.2×10^{-2} 7.9×10^{-2}
I) Hexafluorohafnates	Ammonium hexafluorohafnate Lithium hexafluorohafnate Sodium hexafluorohafnate Potassium hexafluorohafnate Rubidium hexafluorohafnate Cesium hexafluorohafnate	1×10^0 1×10^{-1} 7×10^{-2} 1.3×10^{-1} 1.9×10^{-1} 1.7×10^{-1}
J) Hexafluorogallates	Ammonium fluorogallate Alkali/Alkaline fluorogallates Silver (I) fluorogallate Copper (II) fluorogallate Zinc fluorogallate Manganese (II), iron (II), and cobalt (II) fluorogallates	1×10^{-2} 1×10^{-2} 1×10^0 1×10^{-2} 1×10^{-1} 1×10^{-2}

K) Hexafluorophosphates	Ammonium hexafluorophosphate Lithium hexafluorophosphate Sodium hexafluorophosphate Potassium hexafluorophosphate Rubidium hexafluorophosphate Cesium hexafluorophosphate	1×10^0 2×10^0 5.6×10^0 5.1×10^{-1} 1×10^{-1} 1×10^{-1}
L) Hexafluoroantimonates	Ammonium hexafluoroantimonate Lithium hexafluoroantimonate Sodium hexafluoroantimonate Potassium hexafluoroantimonate Rubidium hexafluoroantimonate Cesium hexafluoroantimonate	4.7×10^0 1×10^0 4.97×10^0 3.7×10^0 1.6×10^0 5×10^0
M) Heptafluoroniobates	Lithium heptafluoroniobate Sodium heptafluoroniobate Potassium heptafluoroniobate Rubidium heptafluoroniobate Cesium heptafluoroniobate	5×10^{-1} 5×10^{-2} 2.6×10^{-1} 1×10^{-1} 3×10^{-1}
N) Heptafluorotantalates	Lithium heptafluorotantalate Sodium heptafluorotantalate Potassium heptafluorotantalate Rubidium heptafluorotantalate Cesium heptafluorotantalate	5×10^{-1} 5×10^{-2} 3×10^{-1} 1×10^{-1} 3×10^{-1}

The concentration of preparative agent must be sufficient to treat the selected surface because the preparative agent initiates the entire coating process. Low fluoride ion concentrations result in thin coatings that do not exhibit an acceptable degree of corrosion inhibition. The substrate metal remains smooth and bright, and no visible coating action takes place at very low fluoride ion concentrations. These effects were found to begin when the ratio of fluoride ions to cerium ions in the coating solution falls below a ratio of 0.05. Therefore, the minimum recommended fluoride-to-cerium, fluoride-to-praseodymium, or fluoride-to-terbium ratio is 0.05.

10

5) Valence Stabilizer Concentration

The concentration of the valence stabilizer can be any concentration up to the maximum solubility of the specific valence stabilizer source used. Any concentration exceeding this solubility will result in undissolved solid material that will not be available for stabilizing the desired tetravalent cerium, praseodymium, or terbium ions. Since this process was developed to operate at ambient temperature, the concentration of valence stabilizer source should be restricted to its maximum solubility in water at or near ambient temperature (25°C). Higher

temperatures may allow more valence stabilizer to be added to the conversion coating solution, but this is unnecessary and adds additional cost to the process. Table 6 shows the aqueous solubilities of some of the more desirable sources for wide band (typical) inorganic valence stabilizers, and Table 7 shows the aqueous solubilities of some sources for narrow band (less typical) inorganic valence stabilizers.

Table 6
Solubilities of Wide Band Inorganic Valence Stabilizer Precursors
under Ambient Conditions
[Maximum Allowable Concentrations in Solution]
(At or near 25°C and at or near pH 7)

Inorganic Valence Stabilizer	Example Precursors	Solubility in Water (mole/L)
Molybdates	Molybdenum trioxide	7.4×10^{-3}
	Molybdic acid	7.4×10^{-3}
	Ammonium molybdate	5×10^0
	Lithium molybdate	1×10^1
	Sodium molybdate	2.15×10^2
	Potassium molybdate	7.75×10^2
	Rubidium molybdate	6.4×10^0
	Cesium molybdate	4.8×10^0
	Magnesium molybdate	7.4×10^{-1}
Tungstates	Tungstic acid	8.0×10^{-1}
	Ammonium tungstate	1×10^2
	Lithium tungstate	5.8×10^1
	Sodium tungstate	2.49×10^2
	Potassium tungstate	1.42×10^2
	Rubidium tungstate	5×10^1
	Cesium tungstate	5×10^0
	Magnesium tungstate hydrate	7.2×10^{-1}
Vanadates	Vanadium pentoxide	4.4×10^{-2}
	Ammonium vanadate	4.4×10^{-2}
	Lithium vanadate	1×10^0
	Sodium vanadate	1.7×10^0
	Potassium vanadate	1×10^0
	Rubidium vanadate	5×10^{-1}
	Cesium vanadate	5×10^{-1}
	Magnesium vanadate	1×10^0
	Calcium vanadate	5×10^{-1}
Niobates	Ammonium niobate	1×10^{-1}
	Lithium niobate	1×10^{-1}
	Sodium niobate	5.9×10^{-2}
	Potassium niobate	5×10^{-2}
	Magnesium hexaniobate	8.8×10^{-2}
	Calcium hexaniobate	4.7×10^{-2}
Tantalates	Ammonium tantalate	1×10^{-2}
	Lithium tantalate	1×10^{-2}

	Sodium tantalate Potassium tantalate	5.5×10^{-3} 5×10^{-3}
Tellurates	Telluric acid Ammonium tellurate Lithium tellurate Sodium tellurate Potassium tellurate Rubidium tellurate Cesium tellurate	5×10^{-1} 5×10^{-1} 1×10^0 2.8×10^{-2} 1×10^{-2} 1×10^{-2} 1×10^{-2}
Periodates	Periodic acid Ammonium periodate Lithium periodate Sodium periodate Potassium periodate Rubidium periodate Cesium periodate Magnesium periodate	4.96×10^1 1.3×10^{-1} 5×10^1 6.7×10^{-1} 2.9×10^{-2} 2.4×10^{-2} 6.6×10^{-2} 5×10^0
Antimonates	Ammonium antimonate Lithium antimonate Sodium antimonate Potassium antimonate Rubidium antimonate Cesium antimonate	1×10^0 1×10^0 1.2×10^{-3} 1.04×10^{-1} 1×10^{-1} 5×10^{-2}
Stannates	Ammonium stannate Lithium stannate Sodium stannate Potassium stannate Rubidium stannate Cesium stannate	5×10^0 5×10^0 2.3×10^0 3.7×10^0 5×10^0 1×10^0
Iodates	Iodic acid Iodine pentoxide Ammonium iodate Lithium iodate Sodium iodate Potassium iodate Rubidium iodate Cesium iodate Magnesium iodate	1.76×10^1 5.6×10^0 1×10^{-1} 4.4×10^0 4.5×10^{-1} 2.2×10^{-1} 8.1×10^{-2} 8.4×10^{-2} 2.29×10^{-1}
Phosphates	Phosphoric acid Ammonium phosphate Lithium phosphate Sodium phosphate Potassium phosphate Pyrophosphoric acid Sodium pyrophosphate	5.6×10^1 1.3×10^0 3.4×10^{-3} 2.6×10^{-1} 4.2×10^0 4.0×10^1 1.2×10^{-1}
Bromates	Ammonium bromate Lithium bromate Sodium bromate Potassium bromate Rubidium bromate Cesium bromate Magnesium bromate Calcium bromate Strontium bromate	1×10^1 4.85×10^0 1.82×10^0 8.0×10^{-1} 1.4×10^{-1} 1.4×10^{-1} 1.0×10^0 1×10^0 9.1×10^{-1}

	Zinc bromate Ferric bromate	1×10^0 $\sim 1 \times 10^0$
Nitrates	Nitric acid	75 wt. %
	Ammonium nitrate	2.5×10^1
	Lithium nitrate	1.3×10^1
	Sodium nitrate	1.1×10^1
	Potassium nitrate	7.4×10^0
	Rubidium nitrate	3.0×10^0
	Cesium nitrate	2.1×10^0
	Magnesium nitrate	4.9×10^0
	Calcium nitrate	2.1×10^1
	Strontium nitrate	3.4×10^0
	Zinc nitrate	6.2×10^0
	Barium nitrate	3.3×10^{-1}
	Aluminum nitrate	1.7×10^0
	Ferric nitrate	5.7×10^0
	Tetramethylammonium nitrate	$\sim 1 \times 10^1$
	Tetraethylammonium nitrate	$\sim 5 \times 10^0$
	Tetrapropylammonium nitrate	$\sim 1 \times 10^0$
	Tetrabutylammonium nitrate	$\sim 5 \times 10^{-1}$
Sulfates	Sulfuric acid	75 wt. %
	Ammonium sulfate	6.1×10^0
	Lithium sulfate	2.7×10^0
	Sodium sulfate	2.2×10^0
	Potassium sulfate	1.0×10^0
	Rubidium sulfate	1.7×10^0
	Cesium sulfate	5.0×10^0
	Magnesium sulfate	3.0×10^0
	Zinc sulfate	3.4×10^0
	Aluminum sulfate	3.0×10^0
Carbonates	Ferric sulfate	7.9×10^0
	Ammonium carbonate	8.8×10^0
	Ammonium bicarbonate	1.5×10^0
	Lithium carbonate	2.1×10^{-1}
	Lithium bicarbonate	8.1×10^{-1}
	Sodium carbonate	7.5×10^{-1}
	Sodium bicarbonate	8.2×10^{-1}
	Potassium carbonate	8.1×10^0
	Potassium bicarbonate	3.9×10^0
	Rubidium carbonate	1.95×10^1
	Rubidium bicarbonate	3.7×10^0
	Cesium carbonate	8.0×10^0

Table 7
Solubilities of Narrow Band Inorganic Valence Stabilizer Precursors
under Ambient Conditions
(Maximum concentration in solution at or near 25°C and pH 7)

5

Narrow Band Inorganic Valence Stabilizer	Example Precursors	Solubility in Water (mole/L)
A) Germanates	Germanium dioxide hydrate	4.3×10^{-2}
	Ammonium germanate	$\sim 1 \times 10^0$
	Lithium germanate	6.3×10^{-2}
	Sodium germanate	1.55×10^0
	Potassium germanate	$\sim 1 \times 10^0$
	Rubidium germanate	$\sim 5 \times 10^{-1}$
	Cesium germanate	$\sim 5 \times 10^{-2}$
B) Titanates	Titanium hydroxide	1.36×10^{-4}
C) Zirconates	Zirconium hydroxide	1.26×10^{-3}
D) Selenates	Selenic acid	60 wt. %
	Ammonium selenate	6.0×10^0
	Sodium selenate	1.2×10^0
	Potassium selenate	5.0×10^0
E) Bismuthates	Bismuth nitrate	2.7×10^{-2}
	Bismuthyl perchlorate	$\sim 1 \times 10^{-1}$
F) Arsenates	Arsenic pentoxide	6.5×10^0
	Ammonium arsenate	2.1×10^0
	Sodium arsenate	9.2×10^{-1}
	Potassium arsenate	7.4×10^{-1}
G) Silicates	Sodium silicate	$\sim 1 \times 10^0$
	Potassium silicate	$\sim 1 \times 10^0$
H) Borates	Boric acid	1×10^0
	Ammonium borate	2.8×10^{-1}
	Lithium borate	5.2×10^{-1}
	Sodium borate	3.9×10^0
	Potassium borate	8.7×10^0
I) Aluminates	Sodium aluminate	$\sim 1 \times 10^0$
	Potassium aluminate	$\sim 1 \times 10^0$

10

The number of complexing octahedra or icosahedra around the central Ce^{+4} , Pr^{+4} , or Tb^{+4} ion varies from species to species (e.g., molybdates vs. tungstates). Varying the concentration of the complexing agent while keeping the Ce^{+4} , Pr^{+4} , or Tb^{+4} concentration constant resulted in clear differences in corrosion protection. The degree of corrosion protection was found to fall off dramatically below a valence stabilizer-to-cerium ratio of about 0.01. Therefore, the minimum recommended valence stabilizer-to-cerium, valence stabilizer-to-praseodymium, or valence stabilizer-to-terbium ratio is 0.010, with ratios higher than 0.015 being typical.

15

The maximum concentration of organic valence stabilizers is dependent upon the precursor solubility. Because of the very large number of potential organic valence stabilizers,

precursor solubilities are not shown. The minimum concentration of valence stabilizer is dependent upon the specific Ce⁺⁴-, Pr⁺⁴-, or Tb⁺⁴-valence stabilizer complex being formed within the conversion coating. The solubility and maximum solution concentration of these materials also increases with temperature, but this increased temperature is unnecessary to produce an effective coating.

5 6) Solubility Control Agent Concentration

The concentration of the optional solubility control agent can be any concentration up to its maximum solubility under ambient conditions. Exceeding the solubility will result in undissolved solid material that will not be available for adjusting the solubility of the cerium-, praseodymium-, or terbium-stabilizer complex. The solubilities of potential solubility control agents are not shown because of the large number of cationic or anionic species which can be used. Standard values for the solubilities of these materials in water can be used as the maximum allowable concentrations in the prepared solutions.

10 7) Coating Solution pH

The conversion coating solution should have an acidic or neutral pH so that a rise in pH caused by oxide and metal dissolution from the work surface will result in a rise in local pH and the precipitation of the desired conversion coating materials. Solution pH must not be so low that the pH rise during the conversion coating process is insufficient to result in coating precipitation. Very low pH values in the conversion coating solutions may also lead to excessive substrate metal loss and possible hydrogen embrittlement of the work piece.

The maximum practical pH of the conversion coating solution is about 7 and the lowest practical pH is -1.5 for tetravalent cerium, praseodymium, or terbium coating application. Optimally, however, the pH should not be higher than 6 or less than 1 or 2. The pH of the tetravalent cerium, praseodymium, or terbium conversion coating solutions should be checked periodically to confirm that it falls within operational parameters. Separate solutions that contain either valence stabilizers or optional solubility control agents generally do not require careful pH control.

8) Redox Potential of the Coating Solution

The necessary redox potential of the conversion coating solution is a function of both the solution pH and the cerium, praseodymium, or terbium concentration. Approximate values for the necessary redox potential of the solution for cerium can be derived from the Pourbaix stability diagram for cerium. These values are shown in Table 8. Tetravalent cerium may be produced in solution at slightly lower redox values than those in Table 8 if the cerium is already complexed with suitable valence stabilizers. Tetravalent praseodymium or terbium may also be formed in a coating, provided that the redox potential is sufficiently high, and that the optimum valence stabilizer for Pr^{+4} or Tb^{+4} is used. An approximate value of the necessary redox potential for Pr^{+4} or Tb^{+4} can be derived by adding 0.3 to 0.4 V to those shown in Table 8.

Table 8
Approximate Redox Potential as a
Function of Conversion Coating Solution pH

pH	Minimum Redox Potential (V)
0	1.7
1	1.6
2	1.5
3	1.3
4	1.1
5	1.0
6	0.8
7	0.7

These redox potentials can be achieved through chemical (or electrochemical) means. The redox potential of the conversion coating solution will slowly drop over a period of several days. It should be brought back up to those values shown in Table 8 when this happens. Periodic evaluation of the redox potential of these solutions can be performed using ASTM D-1498 (Oxidation-Reduction Potential of Water) or comparable test procedures. Post-treatment solutions that contain valence stabilizers or optional additional solubility control agents generally do not require control of the redox potential.

9) Application Temperature

The recommended application temperature range of the conversion coating solution is between 5 and 40°C, with temperatures at or near ambient (20 to 25°C) being typical.

Application temperatures that are cooler than the typical range will result in a much slower coating deposition rate and may result in incomplete film formation. Temperatures higher than ambient can be used, but this is unnecessary and can increase the cost and application difficulty associated with the process. A temperature range of between about 5 and about 100°C therefore constitutes the maximum allowable range for the application of these processes.

5 10) Contact Time, Coating Thickness

The contact time for the solutions should be sufficient to allow the formation of a uniform conversion coating of sufficient thickness to be effective as both a barrier film and a reservoir of Ce⁺⁴, Pr⁺⁴, or Tb⁺⁴ corrosion inhibitor. An average time of about 5 minutes has been found effective. A minimum solution contact time has been found to be about 1 minute under ambient conditions. Contact times will vary with parameters including solution concentrations, temperature, pH, and alloy composition. The barrier oxide film needs to develop long enough to provide a suitable base for mechanical adhesion of a later paint layer. Incomplete coating deposition will result in coatings with reduced mechanical adhesion. A satisfactory conversion coating has a combination of coating thickness and coating morphology that provides for good adherence of the conversion coating as well as to subsequently applied paints and coatings. The state-of-the-art chromium conversion coatings exhibit a coating thickness of approximately 200 nanometers, as well as a “mud-crack” or “honeycomb” morphology. Thinner coatings may be acceptable, but their morphology must be enhanced to achieve comparable paint adhesion. The minimum thickness of a tetravalent cerium, praseodymium, or terbium coating will vary with substrate composition. A lower limit will be approximately 25 nanometers to form a pin-hole free uniform coating that will promote paint adhesion. Conversely, very thick conversion coatings can result in low mechanical adhesion due to fracture through the grown films. The maximum thickness for a satisfactory tetravalent cerium, praseodymium, or terbium conversion coating is approximately 10,000 nanometers.

20 C) GENERAL APPLICATION PROCESS

The general process flow diagram for the application of the optimized tetravalent cerium, praseodymium, or terbium conversion coatings is as follows:

- 25 1) Precleaning (if required)

- 2) Masking (if required)
- 3) Alkaline cleaning/rinsing (if required)
- 4) Deoxidizing/rinsing (if required)
- 5) Formation of optimized tetravalent cerium, praseodymium, or terbium conversion coating
- 6) Rinsing
- 7) Post-coating treatment
- 8) Rinsing
- 9) Drying (if required).

10

Each of these processing steps are discussed briefly as follows:

- 1) Precleaning (if required)

Oils or greases on the part to be coated are removed using an appropriate technique, such as vapor degreasing.

15

- 2) Masking (if required)

Any areas that are not to be conversion coated with the cerium, praseodymium, or terbium conversion coatings are masked off using appropriate maskants. Any system component which may be adversely affected by the cerium, praseodymium, or terbium conversion coating process should also be masked off.

20

- 3) Alkaline Cleaning/Rinsing or Other Cleaning Process (if required)

Alkaline cleaning is suggested to remove traces of oils or hydrocarbon contaminants on the metal surface. These alkaline cleaning solutions frequently need elevated temperatures for application. The metal piece should be rinsed thoroughly following alkaline cleaning.

25

- 4) Deoxidizing/Rinsing (if required)

30

Deoxidizing should be performed using appropriate deoxidizing solutions in accordance with performance specifications in order to remove the natural oxide film on the surface of the metal piece. Following deoxidizing, the metal piece is thoroughly rinsed while reducing as much drag-out as possible from the deoxidizing bath.

5) Formation of Cerium, Praseodymium, or Terbium Conversion Coating

The conversion coating solution (as described above) is applied through immersion, spray application, fogging, or manual application.

5 6) Rinsing

Standard rinse procedures are used.

7) Post-Coating Treatment

Solution formulations can be developed where a valence stabilizer is not included in the initial conversion coating solution or additional solubility control agents are needed to modify compounds formed during coating deposition. A second solution application (either by immersion, spray application, fogging, or manual application) may be necessary. This second solution would contain the cerium, praseodymium, or terbium valence stabilizer or solubility control agent.

15 Post coating treatments to the formed conversion coating can also include treatments to change the color of the formed coating through the action of dyes or bleaching agents. For example, thick hexavalent chromium conversion coatings on zinc are often dyed black from the original olive-drab color as-formed on the galvanized work piece. Likewise, bleaching agents are applied to hexavalent chromium conversion coatings on zinc to obtain a clear or iridescent effect. The application of dyes or bleaching agents to conversion coatings based on tetravalent cerium, praseodymium, or terbium will change the color of these coatings also. Brighteners include such materials as sulfonic acids, sulfonates, sulfonamides, sulfinic acids, sulfinites, sulfones, cyanides, and nonionic surfactants.

25 8) Rinsing

Standard rinse procedures are used.

9) Drying (if required)

30 Standard drying methods may be used. The state-of-the-art hexavalent chromium coatings require a 24-hour “aging” period prior to paint application. Comparable “aging” is optional but typical for cerium, praseodymium, or terbium conversion coatings.

Examples

In order that the invention may be more readily understood, reference is made to the following examples, which are intended to illustrate the invention, but not limit the scope thereof. Moreover, these examples are not intended to represent refined final commercial compositions. They are intended to demonstrate the range and robustness of the Ce⁺⁴, Pr⁺⁴, and Tb⁺⁴ valence stabilization for conversion coatings of the present invention.

We present first the conditions by which many of our examples were formed, the conditions under which their corrosion resistance was tested, and the color exhibited by many of the example tetravalent cerium conversion coatings. We then present some comparative examples of prior art references that were examined during the development program associated with the present application. Finally, some examples using either inorganic or organic valence stabilizers with Ce⁺⁴ are discussed.

1. Stock Solution and Sample Preparation

The test examples explored here (with the exception of the comparative examples) were all prepared in the same manner to avoid preparation and compositional complications during analysis of stabilizer or preparation agent performance. Ammonium cerium nitrate [(NH₄)₂Ce(NO₃)₆] was the compound used for the water-soluble cerium source (although many others could be used). The same quantity of potassium hexafluorozirconate preparative agent was used as is in the CrVI baseline solution.

The following were held constant for all of the conversion coating solution formulations:

Ammonium cerium nitrate	78.9 grams - yielding 0.1440 M CeIV
Potassium hexafluorozirconate	1.70 grams

The reagents were added to one liter of deionized water at room temperature and allowed to dissolve while monitoring solution temperature and pH. Degreased and deoxidized plates of bare 2024-T3 and 7075-T6 aluminum alloys were conversion coated with a specific treatment. Multiple samples of specific compositions were prepared and tested. Exposure results reflect the average combined performance of the specimens rather than a best performance. Ease of use, uniform application methodology, and predictable corrosion-inhibiting performance are emphasized by using multiple samples. The usefulness of these conversion-coating methods depends on the ability to obtain a constant level of corrosion inhibition. Samples treated with

Alodine® 1200 were prepared identically to those used to test CeIV composition variations for purposes of comparison.

Conversion coating performance would be, ideally, independent of the substrate composition. This is not necessarily seen when bare 2024-T3 and 7075-T6 aluminum alloys are tested side-by-side, with either CrVI or CeIV conversion coatings. Substrate composition can influence the effectiveness of a particular conversion coat, but the limited selection of chromate compound solubilities has restricted the general development of application-specific CrVI conversion coatings. The technology presented here will allow the development of both effective wide-spectrum coating systems for general application and tailored coating system solutions for specific needs, all based on tetravalent cerium (praseodymium or terbium).

2. Corrosion Testing

Conversion coat formulations were evaluated by static salt fog (ASTM B-117) and cyclic Prohesion™ (ASTM G-85.5) accelerated corrosion tests. ASTM B-117 is a traditional corrosion proof test, but it has little relation to a real working environment. This accelerated corrosion test exposes samples to a constant salt-water fog and is a *de facto* test of solubility for corrosion inhibitors. B-117 does not necessarily test the ability of a corrosion inhibitor to actually inhibit corrosion. This is particularly true of inhibitors and complexes that have not been fully optimized with respect to solubility. ASTM G-85.5 (Prohesion™) is a cyclic corrosion test that more closely resembles real working environments. This accelerated corrosion test exposes samples to a cycle of fog of dilute salt and ammonium sulfate at room temperature followed by forced-air drying at an elevated temperature. This is a true test of the ability of a compound to inhibit corrosion. Results of these tests may be combined to gain insight into how a particular coating or compound will perform relative to a standard, as well as helping to identify strengths and weaknesses in the performance of a particular material.

3. Color

Coating deposition may be identified by a change in surface texture or color. Commercial CrVI conversion coating systems are known to provide a golden, yellowish (for current systems), or greenish (for older systems) tint to the metal surface after treatment. The usefulness of color in these coatings is as a visual aid during application and as a place marker

after application. The methods of forming conversion coatings described here are capable of producing colored or uncolored corrosion-inhibiting coatings.

4. Comparative Example 1

5 Alodine® 1200 is a commercial CrVI-ferricyanide based conversion coating used extensively to provide corrosion protection to metal surfaces. This material was used as a performance baseline for the effectiveness of CeIV compositions developed using the methodology described herein. Table 9 presents the accelerated corrosion testing results for bare 2024-T3 and 7075-T6 aluminum alloy test panels treated with Alodine® 1200 to form corrosion-
10 inhibiting conversion coatings.

Table 9
Alodine® 1200 Test Results for Accelerated Corrosion

Alloy	B-117 Hours	B-117 Rating	G-85.5 Hours	G-85.5 Rating
2024-T3	98	98%	168	85%
7075-T6	98	100%	168	90%

15 The Alodine® 1200 treated samples performed well during their period of exposure as is expected from the current state-of-the-art. The influence of alloy composition on the performance of the conversion coating became clear over the period of exposure testing.

5. Comparative Example 2

Conversion coating processes based on cerium have been reported in the prior art that make use of oxidation or anodization of cerium-containing solutions. Oxidation of these
20 solutions without the presence of a valence stabilizer will result in the formation of tetravalent cerium oxide, hydrated tetravalent cerium oxide, or tetravalent cerium hydroxide within the formed coating. However, due to their extremely low solubilities, these species provide an insufficient quantity of tetravalent cerium to achieve coating repair. Tetravalent cerium oxide, hydrated tetravalent cerium oxide, or tetravalent cerium hydroxide serve as effective barrier
25 layers until they are breached.

Coating solutions were prepared following the procedure described in U.S. Patent No. 5,192,374; U.S. Patent No. 5,932,083; and PCT International Publication No. WO 88/06639.

For the comparative sample 2-1 (U.S. 5,192,374), a one weight percent solution of lithium nitrate, one weight percent solution of aluminum nitrate, and 0.1 weight percent solution of cerium (III) nitrate were placed into deionized water, the solution was brought to boiling, and cleaned samples of bare 2024-T3 as well as 7075-T6 aluminum alloys were immersed for 5 minutes. For comparative example 2-2 (U.S. 5,932,083), 25.6 grams of cerium (III) nitrate was dissolved in a solution comprised of 960 ml deionized water, 960 ml propylene glycol, and 80 ml of 35 wt. % hydrogen peroxide. This solution was also heated to boiling, and precleaned 2024-T3 and 7075-T6 aluminum alloys were immersed for 15 minutes. Finally, a comparative sample 2-3 (WO 88/06639) was prepared by adding 5.8 grams of cerium (III) nitrate to a solution composed of 417 ml deionized water and 83 ml of 35 wt. % hydrogen peroxide. This solution was also heated to near boiling, and the aluminum alloy samples were immersed for 15 minutes. The coated samples were then exposed to ASTM B-117 and G-85 accelerated corrosion test environments. The specimens failed to inhibit corrosion during accelerated corrosion testing in ASTM G-85. Some minor corrosion inhibition was noted in ASTM B-117 due to the barrier film formed by the coating processes. For example, the samples prepared using the procedure described in WO 88/06639 were observed to be slightly more effective on the 7075 aluminum alloy than on the 2024 aluminum sample.

A variation of this process was also examined (i.e., PCT International Publication No. WO 01/38225) wherein finely divided tetravalent cerium oxide polishing powders were placed into deionized water to form a colloidal suspension. The aluminum species noted above were placed into these solutions at both room and elevated temperatures. The coated samples were exposed to ASTM B-117 and G-85 accelerated corrosion test environments. The specimens failed to inhibit corrosion during accelerated corrosion testing in ASTM G-85. Some minor corrosion inhibition was noted in ASTM B-117 due to the barrier film formed by the coating processes. Depending on the size of the added tetravalent cerium oxide particles, minor deviations in performance could be observed in ASTM B-117.

Detailed analysis of the prior art process (WO 01/38225) determined that heating the coating solutions in the presence of oxidizer was a method of producing a tetravalent cerium oxide barrier coating. However, the oxides that form from the high temperature solution described in this prior art reference will be starved of available CeIV due to the extremely low solubilities of these species.

6. Comparative Example 3.

Polymers or other film-formers (i.e., silicon-based materials) have been used in prior art conversion coating solutions in association with cerium (i.e., European Application No. EP 0 792 922 A1). Film-formers may enhance short-term corrosion resistance by functioning as a barrier layer. CeIV-based conversion coating solutions of proven effectiveness were prepared with film forming additives. A periodate 2x valence stabilized CeIV conversion coating solution was mixed with a polyvinyl butyral resin with an acid diluent and applied to test specimens. The CeIV-periodate valence stabilizer system yields a good conversion coating. Likewise, a molybdate-cerium conversion coating was mixed with a non-inhibitive film former (available from Zip Chem Products, Indianapolis, IN) and applied to test specimens. The deposited periodate/polyvinyl butyral resin film had a low viscosity and did not set up as a film for two days after solution application. Table 10 shows the results of accelerated corrosion testing on this barrier film system.

15

Table 10
Exposure Results for Barrier Film CeIV Formulations

Stabilizer	2024-T3 B-117 135 hrs.	7075-76 B-117 135 hrs.	2024-T3 G-85 135 hrs.	7075-T6 G-85 135 hrs.
Periodate 2x in polyvinyl butyral resin	12%	12%	55%	20%
Periodate 2x in polyvinyl butyral resin	12%	12%	55%	20%

The molybdate-cerium conversion coating that was mixed with a non-inhibitive film former never set and remained liquid 2 weeks after application.

Detailed analysis of the prior art process determined that the film formers interfere with substrate oxidation during the conversion coating process. Thin, incompletely anodized surfaces are formed that restrict the incorporation of a reservoir for active corrosion inhibitor. A comparison of these results with periodate compositions with no polymer indicates that the compositions with no polymer exhibit much greater corrosion resistance.

7. Comparative Example 4

Conversion coating processes based on cerium have been reported in the prior art that make use of electrolysis of cerium-containing solutions. Electrolysis of these solutions without the presence of a valence stabilizer will result in the formation of tetravalent cerium oxide, 5 hydrated tetravalent cerium oxide, or tetravalent cerium hydroxide within the formed coating. Due to their extremely low solubilities, these species provide an insufficient quantity of tetravalent cerium to achieve coating repair. Tetravalent cerium oxide, hydrated tetravalent cerium oxide, or tetravalent cerium hydroxide serve as effective barrier layers until they are breached.

10 Coating solutions were prepared following the procedure described in U.S. Patent No. 5,194,138. For the comparative sample 4-1, two solutions comprised of 2.18 grams of cerium (III) nitrate dissolved in 500 ml deionized water and 2.0 grams of cerium (III) chloride dissolved in 500 ml deionized water were prepared. When in use, these solutions were heated to 80°C. Precleaned 2024-T3 and 7075-T6 aluminum samples were immersed in the heated cerium nitrate 15 solution for one hour followed by one hour in the heated cerium chloride solution. For comparative example 4-2, a third solution composed of 10.3 grams sodium molybdate in 500 ml deionized water was also prepared and heated to 80°C. For comparative example 4-2, the precleaned aluminum pieces were immersed in solutions one and two for the allotted time at the required temperature, then transferred to the third solution where a constant potential 500 mV 20 more positive than the aluminum samples was applied for one hour. A third coating process (4-3), not specified in the prior art, was performed by electrolyzing the aluminum samples in the prepared cerium (III) nitrate solutions for one hour at 80°C. The coated samples were exposed to ASTM B-117 and G-85 accelerated corrosion test environments. The specimens failed to inhibit corrosion during accelerated corrosion testing in ASTM G-85. Some minor corrosion inhibition 25 was noted in ASTM B-117 due to the barrier film formed by the coating processes. Slightly higher corrosion resistance in ASTM G-85 was noted for the samples that had been electrolyzed in the molybdate solution.

30 Detailed analysis of the prior art process determined that electrolyzing the coating solutions in the presence of oxidizer was a method of producing a tetravalent cerium oxide barrier coating. However, the oxides that form from high temperature solution in this prior art reference will be starved of available CeIV due to the extremely low solubilities of these species.

Subsequent electrolysis in a molybdate solution produced minor amounts of a cerium (IV) molybdate species on the exterior of the formed coating. Because the majority of the deposited cerium was deposited in the form of an insoluble cerium (IV) oxide, and because the quantity of cerium (IV) molybdate produced was relatively small (only on the exterior of the coating), only limited corrosion resistance was observed.

5 8. Example 1. CeIV Solubility Range

Three factors influence the effectiveness of CeIV complexes as active corrosion inhibitors. These factors are the solubility, valence stabilization, and polar character of the 10 formed complex. Valence stabilization is necessary for the formation of useful inhibitors. The complex will simply not be able to oxidize surface flaws if the valence is not stabilized. The polar character of the complex is an important but not an essential feature of a corrosion-inhibiting complex.

Complexes lacking significant electrostatic double layer formation are still able to 15 provide some amount of active inhibition. CeIV complex availability is second only to valence stabilization in a conversion coating's ability to provide effective inhibition. The solubility of solid CeIV complexes controls both how much and how fast corrosion inhibitor is supplied to a corroding surface. Solubility ranges for inhibitors have been referred to as insoluble, sparingly soluble, and very soluble. Sparingly soluble compounds are known to offer the widest range of 20 useful oxidizer in solution.

A test to identify the range of CeIV availability in solution needed to inhibit corrosion was performed by preparing a series of simple complexes with valence stabilization and polar character held constant. Conversion coating solutions containing CeIV as the oxidizing component were prepared where the CeIV ion was valence stabilized in solution with nitrate 25 alone. Six nitrate molecules are known to pack around soluble CeIV forming a hexanitratocerium ($\text{Ce}(\text{NO}_3)_6^{-2}$) complex. The cationic species tetramethylammonium (4 total carbons), tetraethylammonium (8 total carbons), tetrapropylammonium (12 total carbons), tetrabutylammonium (16 total carbons), tetrapentylammonium (20 total carbons), and Adogen 464 (25 total carbons) were used to precipitate $\text{Co}(\text{NO}_3)_6^{-2}$ complexes of varying solubility. 30 Hydroxide was also used to prepare hydrated cerium (IV) oxide- and cerium (IV) hydroxide-containing coatings. Coating solutions containing potassium hexafluorozirconate as a surface

preparative agent were applied to cleaned 2024-T3 aluminum samples. The coated samples were exposed to 135 hours of ASTM B-117 and 135 hours of G-85 accelerated corrosion test environments.

A clear progression of corrosion resistance was observed. $\text{CeO}_2 \cdot x\text{H}_2\text{O}/\text{Ce}(\text{OH})_4$ was precipitated when the hexanitratocerate complex was reacted with hydroxide. The samples containing extremely insoluble $\text{CeO}_2 \cdot x\text{H}_2\text{O}/\text{Ce}(\text{OH})_4$ exhibited little or no corrosion resistance. Samples that contained the more soluble hexanitratocerate species (i.e., tetramethylammonium and tetraethylammonium) performed well in the early stages of the test, but failed to inhibit corrosion part way into the corrosion test. Solubilities as high as about 5×10^{-1} moles/liter of CeIV exhibited corrosion resistance during the early portion of accelerated corrosion testing, but failed later in the test. The higher solubility complexes would have promoted rapid CeIV depletion as the test progressed.

Intermediate solubility complexes of tetrapropylammonium, tetrabutylammonium, and tetrapentylammonium hexanitratocerate species exhibited corrosion resistance greater than tetramethylammonium and tetraethylammonium stabilized complexes and performed the best of this series of stabilizer cations. These exhibited greater corrosion resistance than samples containing tetramethylammonium or tetraethylammonium. This data allowed an approximate range of 5×10^{-2} to 5×10^{-5} moles/liter of CeIV to be established as a typical solubility range for solid CeIV complexes in conversion coatings. Generally, CeIV complex solubility ranges as high as 5×10^{-1} to as low as 1×10^{-5} moles per liter of CeIV, at standard temperature and pressure, may offer some corrosion protection under certain conditions. An approximate solubility range of 5×10^{-2} to 5×10^{-5} moles/liter of CeIV in solution is a desirable solubility range for CeIV in conversion coatings.

It should be noted that we also performed similar tests using deposited CrVI compounds of varying solubility. As with the CeIV coatings, a clear progression of performance based on solubility was observed.

9. Example 2. Inorganic Stabilizers

Inorganic valence stabilizers were used to test and verify the method of forming effective CeIV-based conversion coatings. A series of simple inorganic valence stabilized CeIV complexes were prepared and applied to precleaned bare 2024-T3 and 7075-T6 aluminum alloy

samples. Immersion times were 5 minutes for each piece in each formulation. The coated samples were exposed to ASTM B-117 and G-85 accelerated corrosion test environments. Table 11 shows the type and concentration of each stabilizer that was used in combination with CeIV. The concentration of each stabilizer was either the same as that of ferricyanide in the hexavalent chromium formulations on a molar basis, or, in the case of some of the inorganics, twice that amount. This was done to ensure sufficient source material to form heteropolymetallates for CeIV stabilization within the coating.

Table 11
Formulations and Test Results for Initial CeIV Stabilizers

Stabilizer	Stabilizer Conc.	2024-T3 B-117 65 hrs.	7075-T6 B-117 65 hrs.	2024-T3 G-85 70 hrs.	7075-T6 G-85 70 hrs.
Periodate (Periodic acid)	0.0050 M (1.16 g)	Pass	Pass	Pass	Pass
Tellurate (Telluric acid)	0.0050 M (1.16 g)	Pass	Pass	Pass	Pass
Molybdate (Na molybdate)	0.0100 M (2.32 g)	Pass	Pass	Pass	Pass
Tungstate (Na tungstate)	0.0050 M (0.40 g)	Fail	Fail	Pass	Pass

Pass = 25% or more of all 3 panel surfaces uncorroded

Fail = Less than 25% of all 3 panel surfaces uncorroded.

Three 2024-T3 and three 7075-T6 samples of each formulation were loaded for ASTM B-117 salt fog exposure and ASTM G-85 Prohesion™ exposure. The panels were exposed for 65 hours in the ASTM B-117 Salt fog test and 70 hours in the ASTM G-85 Prohesion™ test - a sufficient time period to begin to see the corrosion resistance of each coating for each alloy.

The periodate, molybdate, and tellurate-stabilized coatings performed well. Some corrosion product formed on this series of samples but all sixteen sample coupons had large bare uncorroded areas. The periodate and molybdate samples exhibited corrosion protection comparable to the Alodine® 1200 treated specimens in both ASTM B-117 and ASTM G-85 environments. The molybdate coatings also exhibited gold coloration, similar to those coatings derived from Alodine® 1200. Other inorganic stabilization agents also were effective to various degrees. The tungstate-stabilized coatings demonstrated the influence of solubility on the performance of the coating during salt fog exposure. This stabilizer is a candidate for further examination to tailor the solubility of the complex with additional solubility control agents.

Solubility control agents were used to modify the solubility of formed compounds. For example, a stock Ce⁺⁴/fluoride solution was prepared using the proportions of ammonium cerium (IV) nitrate and potassium hexafluorozirconate described at the beginning of this section. Second solutions containing both wide band (carbonate, phosphate, antimonite, stannate) and narrow band (silicate) valence stabilizers were prepared. These consisted of 10 grams of phosphoric acid, potassium hexahydroxyantimonate, potassium hydrogen carbonate, or sodium silicate in 1 liter deionized water. A third solution consisting of either 10 grams lithium nitrate or magnesium nitrate in 1 liter deionized water were prepared. The 2024-T3 or 7075-T6 aluminum samples were placed in the first cerium/fluoride solution for 5 minutes at ambient temperature; rinsed; placed into the second solutions containing valence stabilizers for 5 minutes at ambient temperature; rinsed; and then placed into the third solutions containing solubility control agents for 5 minutes at ambient temperatures. The panels were exposed for 100 hours in the ASTM B-117 Salt fog test and 100 hours in the ASTM G-85 Prohesion™ test - a sufficient time period to begin to see the corrosion resistance of each coating for each alloy.

All samples prepared exhibited appreciable corrosion protection. The carbonate-stabilized samples exhibited corrosion protection approaching that of hexavalent chromium. Even the narrow band valence stabilizer (silicate) samples exhibited corrosion protection approaching or equal to hexavalent chromium through the use of these two solubility control agents (Li and Mg).

This set of samples demonstrates the robust character of the method of preparing CeIV-based conversion coatings described herein. Precursor concentration does influence the corrosion resistance of coatings made with these stabilizers. Several of these formulations are of commercial quality with no additional development or refinement necessary. The worst of the chemical systems described work better than current commercial alternatives for CrVI-based conversion coatings. The hexanitrito stabilized compositions could be used immediately as direct equivalent replacements for Alodine® 1200, as well as many of the formulations using lithium or magnesium as solubility control agents. The processes described do not invoke the use of extraneous processing conditions (boiling bath temperatures, applied electric currents) to achieve marginal performance results.

10. Example 3. Organic Valence Stabilizers

Organic valence stabilizers were used to verify the robustness of the method of forming effective CeIV-based conversion coatings. Organic compounds provide an almost unlimited number of possibilities for stabilizer compositions. The encouraging results with inorganic stabilizer compounds suggested the value of examining additional organic stabilizers. The concentration of the organic stabilizers were varied similar to inorganic valence stabilizers shown in the earlier example. Conversion coating solutions were prepared as described above. These solutions were applied to precleaned bare 2024-T3 and 7075-T6 aluminum alloy samples. Immersion times were 5 minutes for each piece in each formulation. The coated samples were exposed to ASTM G-85 accelerated corrosion test environments. Table 12 shows the type and concentration of each organic stabilizer that was used for CeIV.

Table 12
Formulations and Test Results for Organic CeIV Stabilizers

Stabilizer	Stabilizer Conc.	2024-T3 G-85 121 hr min.	7075-T6 G-85 121 hr min.
Ferricyanide 1x (Potassium ferricyanide)	0.0025 M	90%	85%
Flavazin 2x (Flavazin dye)	0.0050 M	95%	80%
Tartrazin 2x (Tartrazin dye)	0.0050 M	95%	80%
Metanil yellow 2x (Metanil dye)	0.0050 M	65%	85%
Phthalocyanine 1x (Phthalocyanine dye)	0.0025 M	65%	20%
Diethyldithiocarbamate 1x	0.0025 M	85%	75%
Biuret 1x	0.0025 M	80%	60%
Naphthol yellow 2x	0.0050 M	90%	80%

The rating numbers correspond to chrome baselines exposed to the same conditions (given a ranking of 100%).

Several of the large organic valence stabilizers approached and passed the level of protection provided by Alodine® 1200 in ASTM G-85 accelerated corrosion testing. Naphthol yellow-, tartrazin-, and flavazin- stabilized CeIV conversion coating performed better than Alodine® 1200 in ASTM G-85 for 2024-T3. The results for salt fog indicate that solubility control is important in tailoring the long-term performance of these compounds. Phthalocyanine, flavazin, and tartrazine were very effective in ASTM G-85 and worked very well for a limited

time in B-117. This result indicates that these materials are effective in inhibiting corrosion but may need additional solubility control to reach their full potential.

5 While the invention has been described by reference to certain embodiments, it should be understood that numerous changes could be made within the spirit and scope of the inventive concepts described. Accordingly, it is intended that the invention not be limited to the disclosed embodiments, but that it have the full scope permitted by the language of the following claims.

We claim: